MATERIALS METROLOGY
IN NANOTECHNOLOGY

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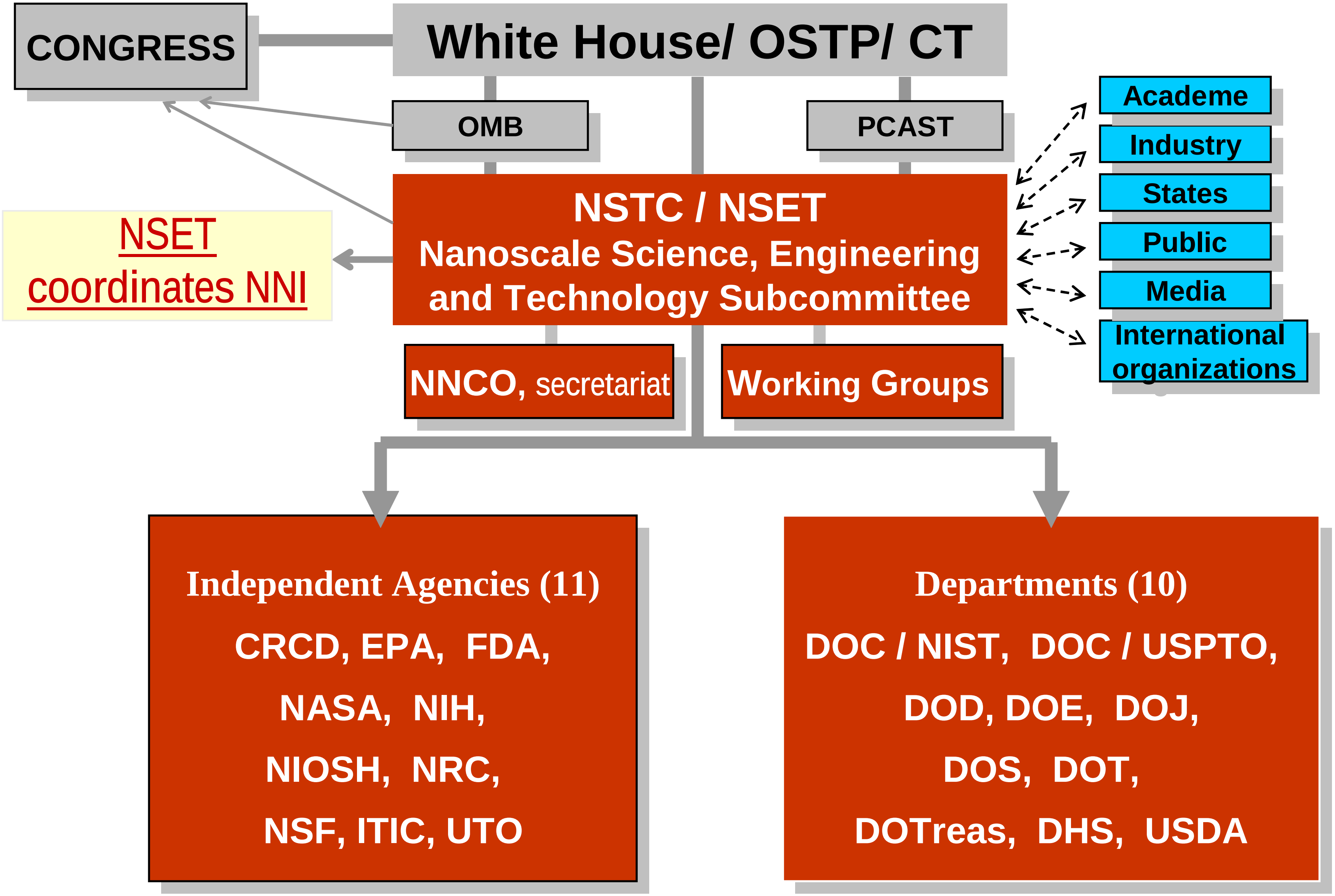
(Member: National Nanoscience
Subcommittee, NSET)



National Nanotechnology Initiative coordination

(Levels: National / Federal agencies, Each agency / Partnerships with industry, states, regional, international / Interaction with public, media)

FUTURE MEETINGS ON NANOSTRUCTURED MATERIALS

September 13-17, 2004
Trends in Nanotechnology (TNT2004), Universidad SEK, Segovia, Spain (Contact: A. Correia, Phantoms, CMP Cientifica, Apdo, Correos 20, 28230 Las Rozas (Madrid), Spain, EMAIL: antonio@phantomsnet.com, WEBSITE: http://www.phantomsnet.com/TNT04/index.php)

September 13-17, 2004
2nd Biennial Symposium and Summer School on Nano and Giga Challenges in Microelectronics Research and Development Opportunites (NGCM2004), Cracow, Poland (Contact: EMAIL: organizers@asdn.net, WEBSITE: http://www.AtomicScaleDesign.Net/ngcm2004)

September 13-17, 2004
6th Yugoslav Materials Society Conference (YUCOMAT 2004), Herceg Novi, Montenegro, Yugoslavia (Contact: D. Uskokovic, FAX: +381-11-185263, EMAIL: uskok@itn.sanu.ac.yu, WEBSITE: http://www.yu-mrs.org.yu)

September 19-21, 2004
4th International Conference on Inorganic Materials, Antwerp, Belgium (Contact: P. Fletcher, EMAIL: phillipa.fletcher@dial.pipex.com, WEBSITE: http://www.im-conference.com)

(CONTINUED ON BACK)

1994 Nobel Prize in Physics

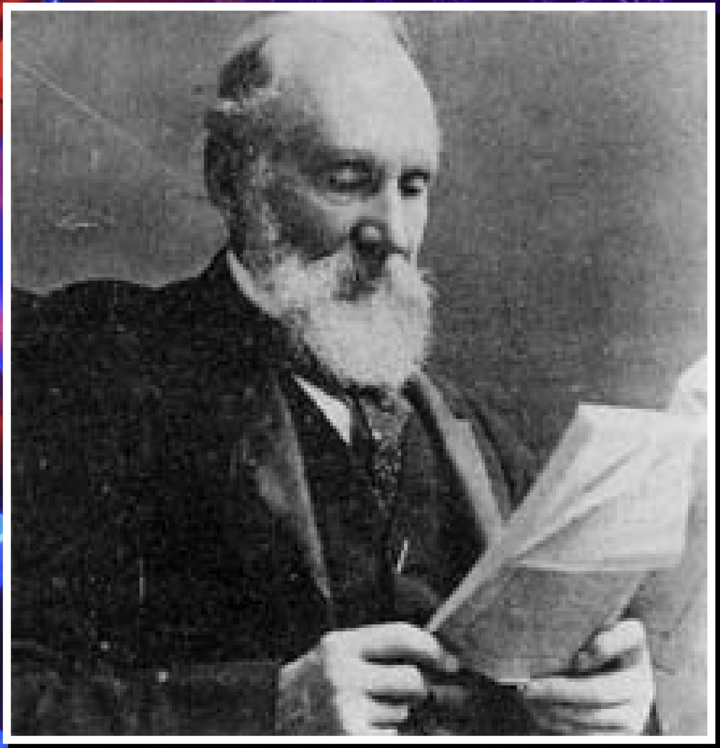
-Pioneer of Neutron Diffraction-

Clifford G. Shull
1915-2001

Swedish King
Carl XVI Gustav

Metrology

The science of measurement; a system of measures



"When you can measure what you are speaking about, you know something about it. But when you cannot measure it, your knowledge is of a meager and unsatisfactory kind. It may be the beginning of knowledge, but you have scarcely advanced to the stage of science."

William Thomson, Lord Kelvin

NIST works closely with government, universities, and industry to develop the Nation's metrology infrastructure necessary for scientific, technical, and economic advances.

OUTLINE

- Why Different Metrology at the Nanoscale?
- Why Properties Change?
- Examples of New Metrology Needs
- NNI Grand Challenge
- NNI Workshop Results on Nanometrology
- NIST Examples

Nanotechnology (what is it?)

- In order to be characterized as nanotechnology by the National Nanotechnology Initiative, work must meet the following criteria:
  - Research and technology development aimed to work at atomic and molecular scales, in the length scale of approximately 1 - 100 nanometer range.
  - Ability to understand, create, and use structures, devices and systems that have fundamentally new properties and functions because of their nanoscale structure.
  - Ability to control – to see, measure, and manipulate matter on the atomic scale to exploit those properties and functions.

Nanotechnology

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  - Research and technology development aimed to work at atomic and mo… …th scale of approximatel… ….
  - Ability to understand, … …, devices and systems that hav… …ally new properties and functions because of their nanoscale structure.
  - Ability to control – to see, measure, and manipulate matter on the atomic scale to exploit those properties and functions.

How do you know?

Nanotechnology

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How do you measure?

Nanotechnology

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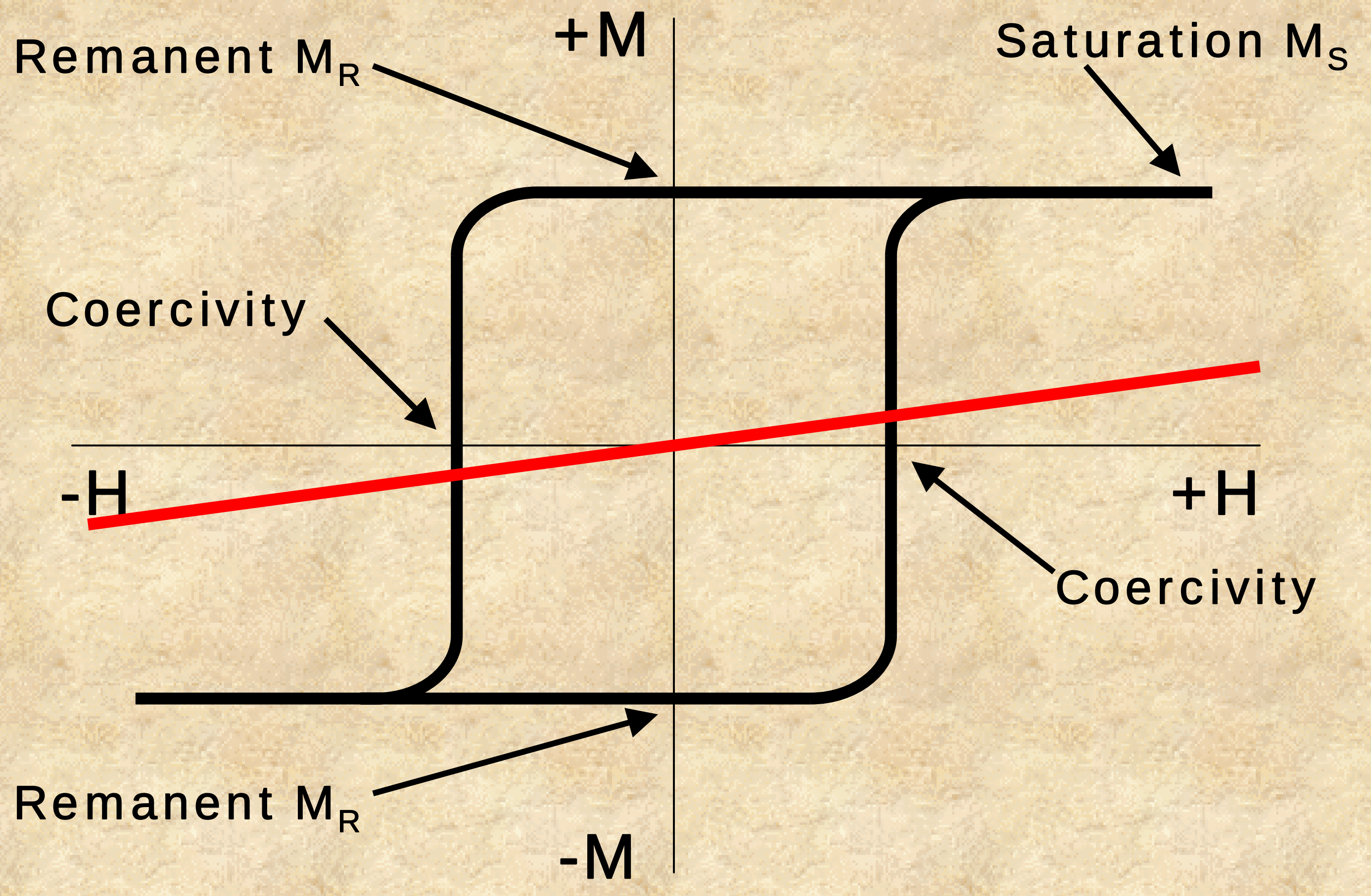
  - Ability to contr … nipulate matter on the a … properties and functions

How do you image or visualize?

MAGNETIC MATERIALS ARE EVERYWHERE!!!

- Magnetic Recording Media, Magnetic Reading and Writing Devices
- ALL Motors
- ALL Transformers
- ALL Generators
- Credit Cards
- Cellular Phones
- Auto & Engine Timing
- Radios & Televisions
- Microwave Devices
- Xerographic Copiers
- Magnetic Separation (Biological Analysis, and Scrap Sorting)
- Magnetic Refrigerators
- Theft Control Devices
- Airport Security
- Permanent Magnets
- Magnetic Fluids
- MRI Contrast Agents
- MF Microscopes
- Motion Control Devices
- Doorbells
- Charging Units
- Fluorescent Lighting

HYSTERESIS LOOP



THREE REASONS

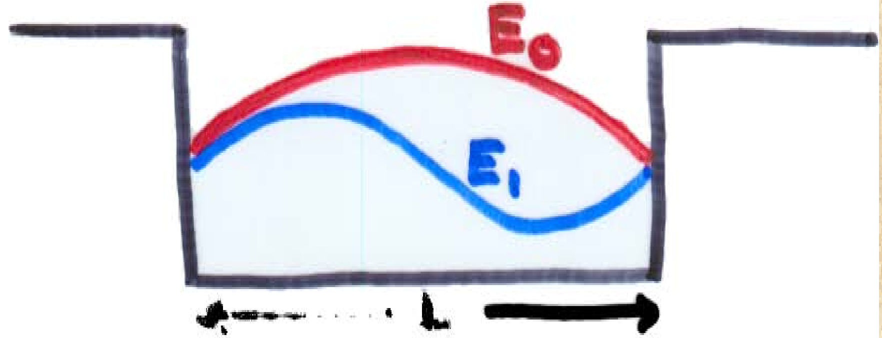
WHY PROPERTIES ARE DIFFERENT

WHEN MATERIALS POSSESS

SOME NANOSCALE DIMENSION

(1)

Quantization of Energy States

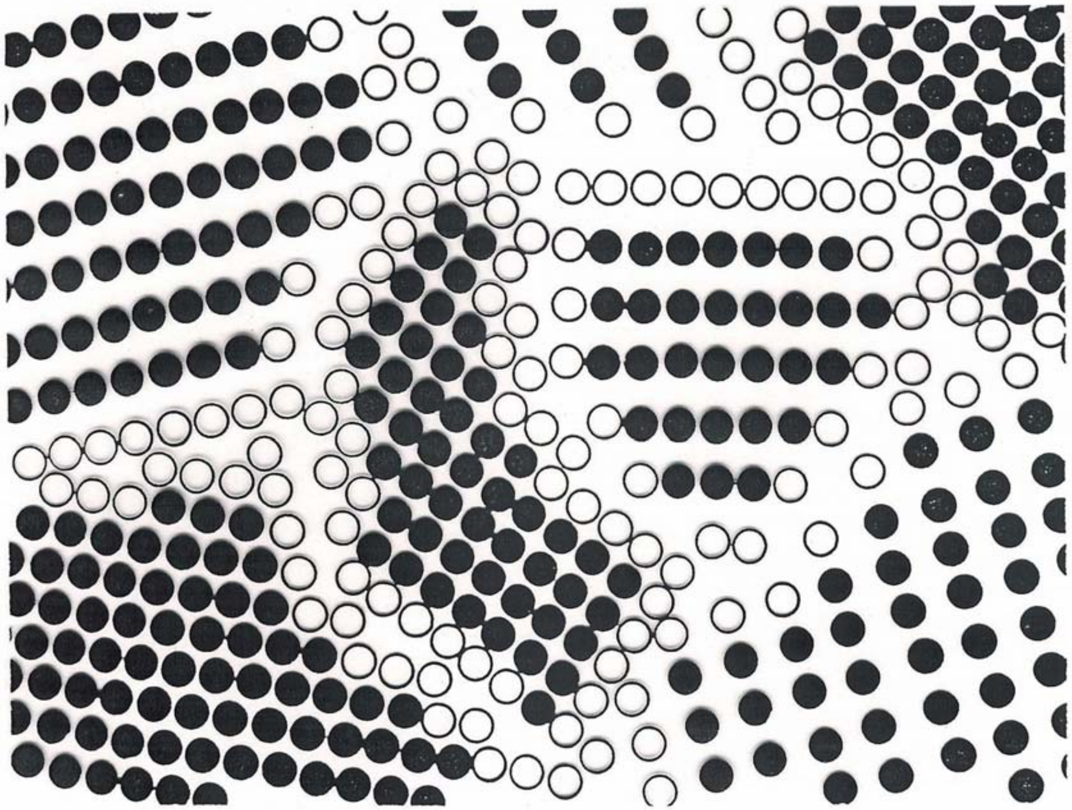


$$E_n = \frac{n^2 C}{L^2}$$

"Confinement" Effects

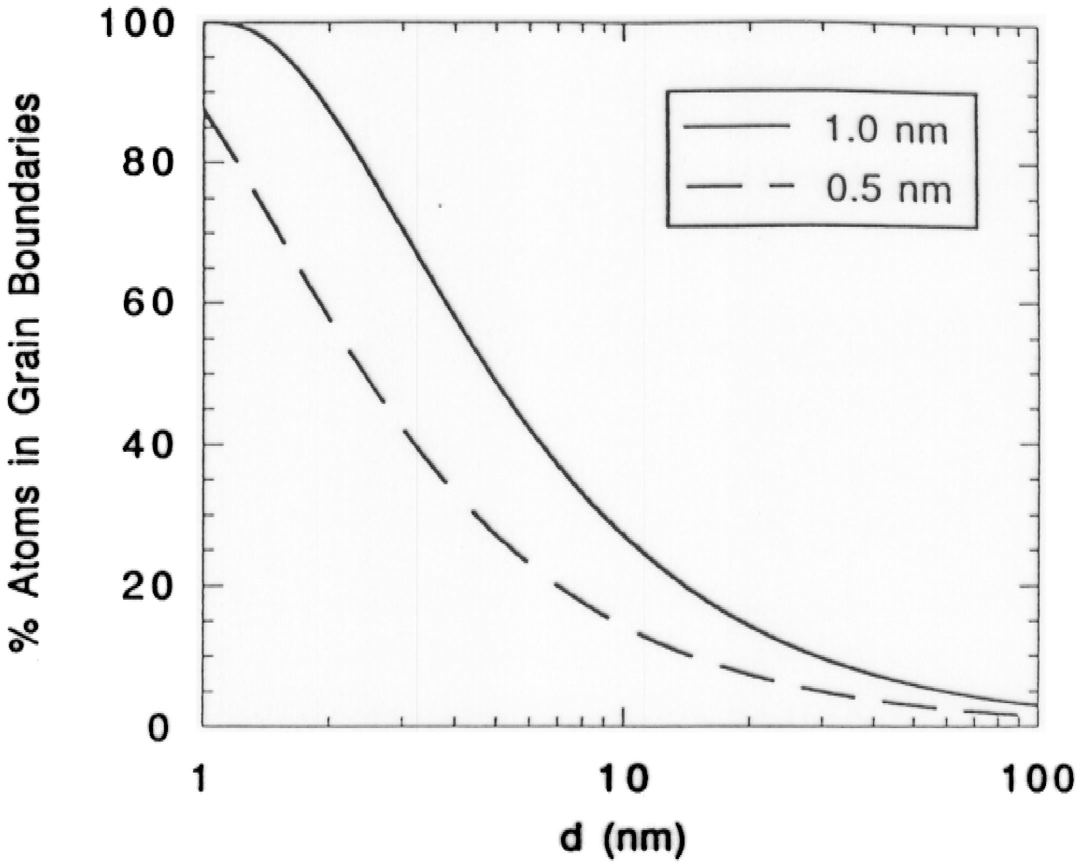
(2)

STRUCTURE SCHEMATIC:
-NANOPHASE MATERIAL-



Schematic of an equiaxed nanocrystalline metal showing atoms associated with individual grains (filled circles) and those constituting the grain boundaries (open circles). [H. Gleiter, Prog. Mater. Sci. 89, 223 (1989)]

HIGH INTERFACE VOLUME
-NANOPHASE MATERIALS-



Percentage of atoms in grain boundaries of a nanophase material as a function of grain diameter, with grain boundary thickness of 0.5 and 1.0 nm (i.e., 2 or 4 atomic planes). [R.W. Siegel, Annu. Rev. Mater. Sci. 21, 559 (1991)]

(3)

CRITICAL LENGTH SCALES

Resistivity – mean free path

Thermal Conductivity – mean free path

Strength – dislocation Burgers vector

Transmission & Reflection - wavelength

Diffraction & Scattering - wavelength

Absorption – penetration depth

Atomic Transport – diffusion length

Superconductivity – coherence length

Elasticity – bond & chain lengths

Reaction Rate – diffusion length

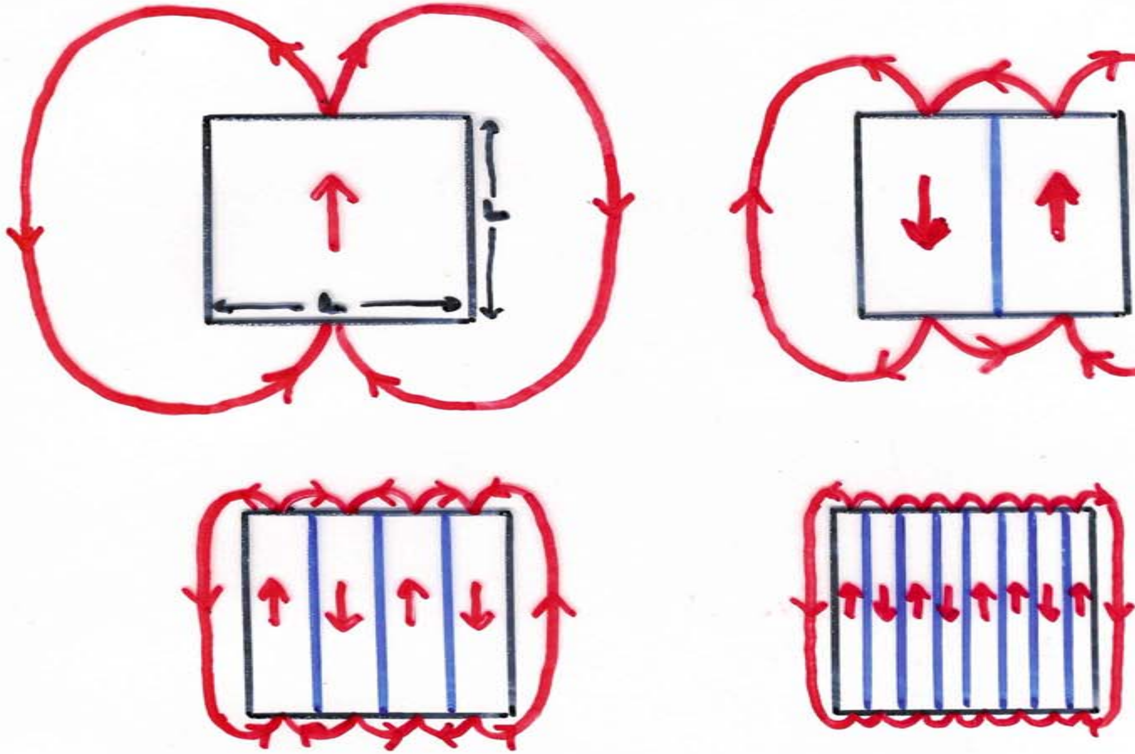
Boundary Motion – radius of curvature

Fluid Flow – boundary layer thickness

MAGNETIC LENGTH SCALES
(IN NANOMETERS)

LENGTH	SYMBOL	DEFINITION	Fe	$Nd_2Fe_{14}B$
Exchange Length	l_{ex}	$\sqrt{(\mu_o A/J_s^2)}$	1.5	1.9
Coherence Radius	R_{coh}	$(\sqrt{24})l_{ex}$	7	9
Domain Wall Width	δ_W	$\pi l_{ex}/\kappa$	40	3.9
Single-Domain Size	R_{SD}	$36\kappa l_{ex}$	6	107
Superparamagnetic Blocking Radius (at 300 K)	R_B	$(6k_BT/K_1)^{1/3}$	8	1.7

DOMAINS



$$E = E_{magnetostatic} + E_{wall}$$

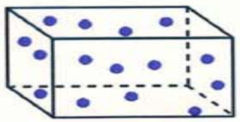
$$= \frac{1}{8\pi} \int_V (H_{ms})^2 \, dV + \gamma_{wall} \frac{L}{t}$$

(t ← thickness)

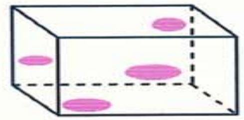
$$\sim L^3 \qquad\qquad \sim L$$

at $\frac{dE}{dL} = 0$ $\quad L_{SD} \leq \frac{1.7}{\pi^2} \frac{\gamma}{M_s^2}$ Single Domain

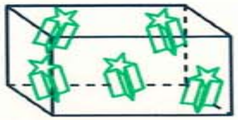
MAGNETIC NANOCOMPOSITES



Spherical particle



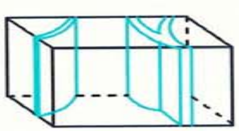
Disk-type particle



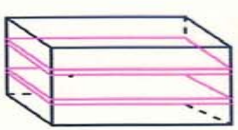
Rod-shaped particle

- Materials possessing a characteristic size scale on the order of $\approx$ 1-20 nm
- For magnetic properties: critical lengths are grain size, magnetic species diameter (+ separation), and magnetic exchange length
- Are Composites of two or more magnetic states; highly composition dependent
- May be single or multiple phase
- Can be prepared from the vapor, from chemical solution, via precipitation, and by deformation
- Possess (1) UNIQUE properties, (2) NEW magnetic states, and (3) UNUSUAL property combinations
- Provide Opportunity for Electronic and Magnetic Engineering

Fiber

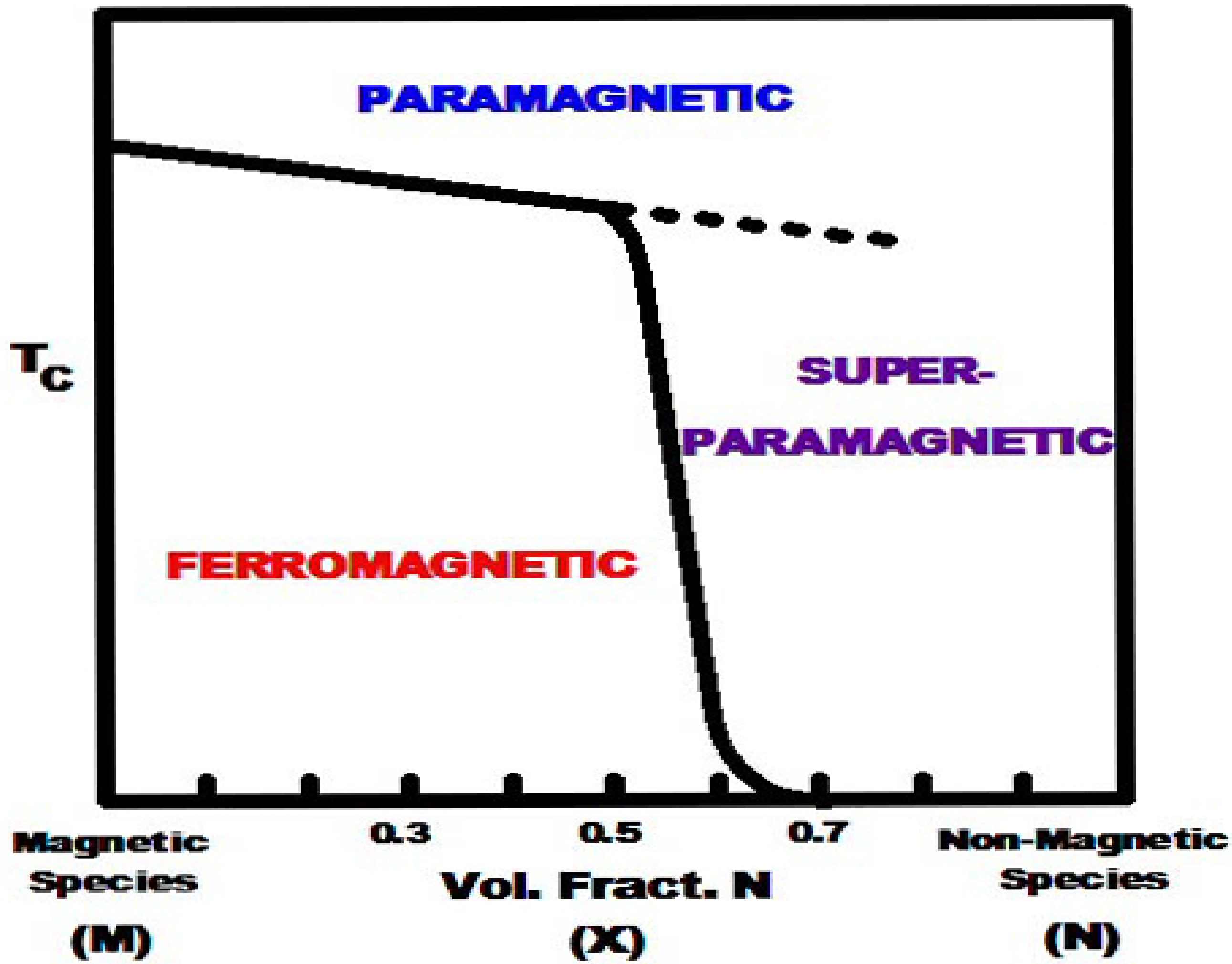


Thin layer

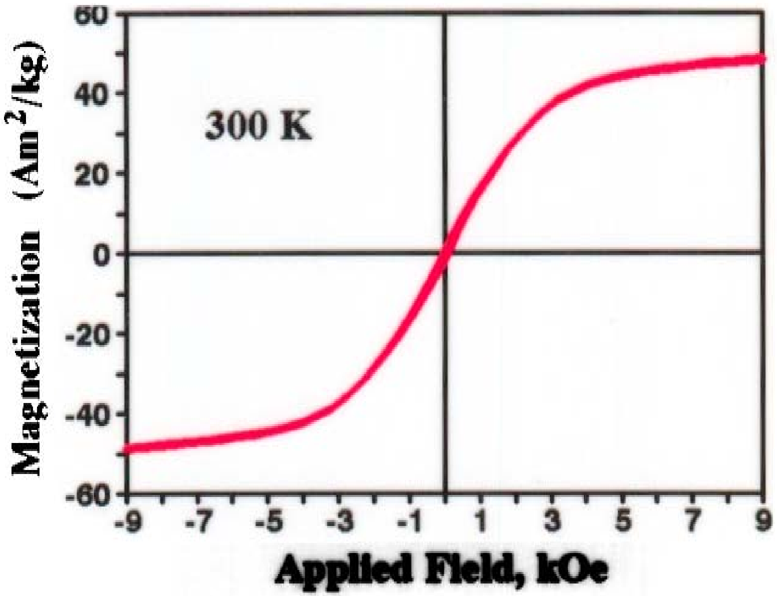


Lamella

NANOCOMPOSITE
($M_{1-x}N_x$)
MAGNETIC PHASE DIAGRAM

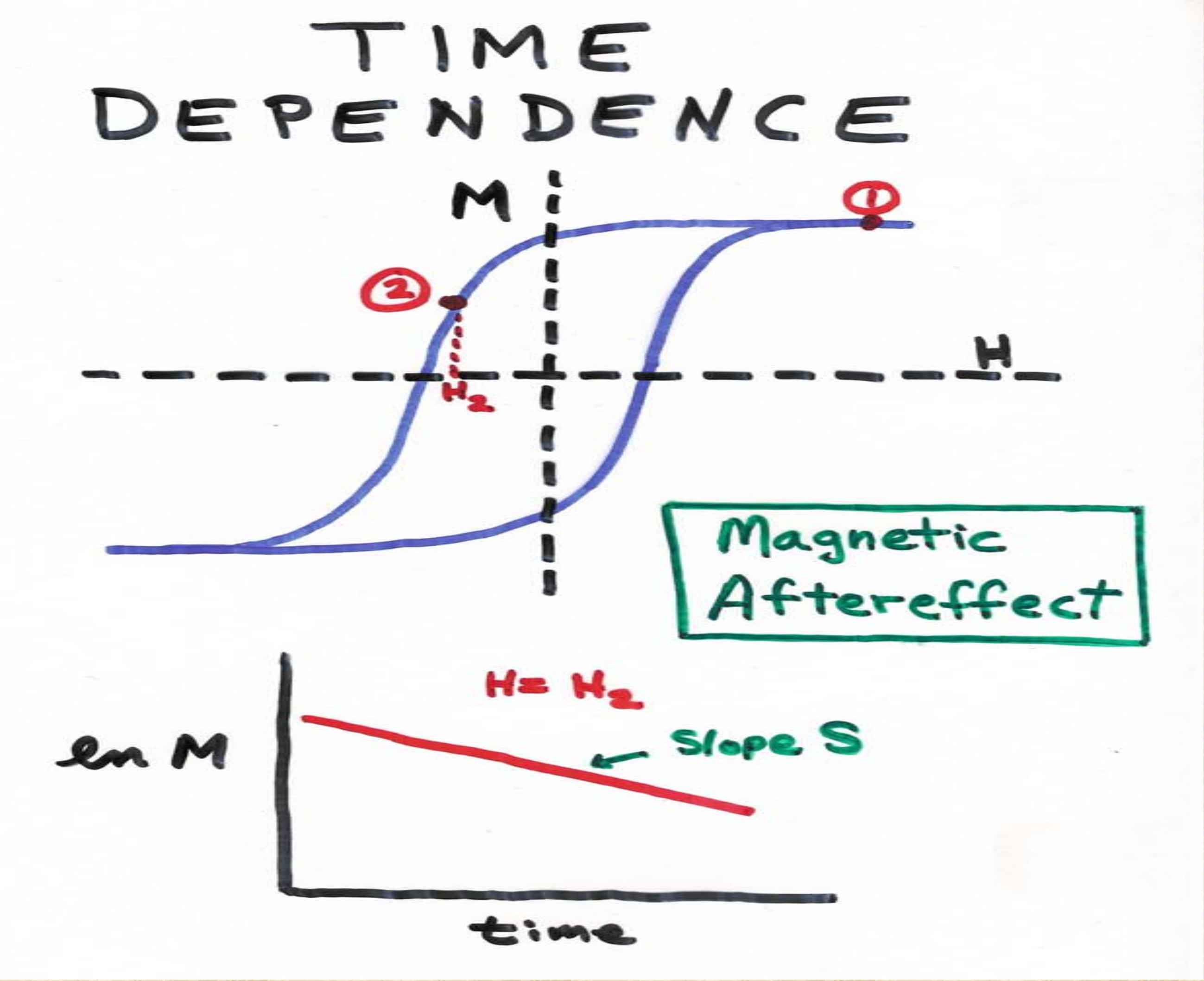


SUPERPARAMAGNETISM

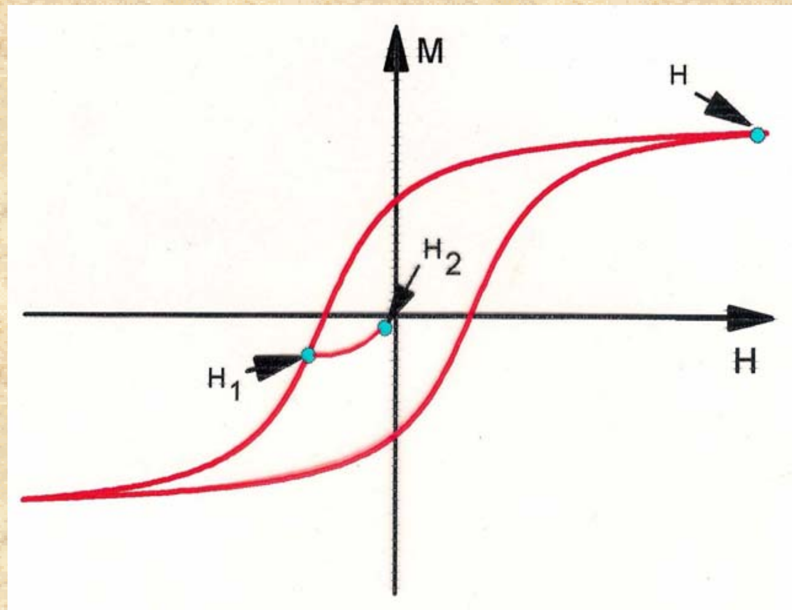


Applications:

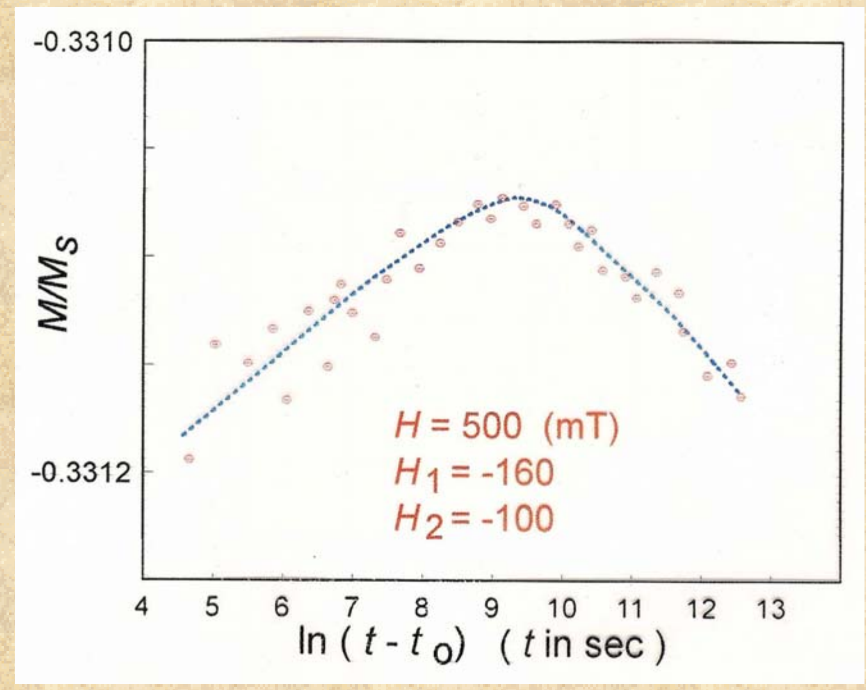
Magnetic Inks
Magnetic Separation
Vacuum Sealing
Magnetic Marking
Magnetic Refrigeration
Magnetic Resonance Imaging


TIME
DEPENDENCE
M
H
1
2
H_2
Magnetic
Aftereffect
H= H_2
ln M
Slope S
time

TIME DEPENDENCE

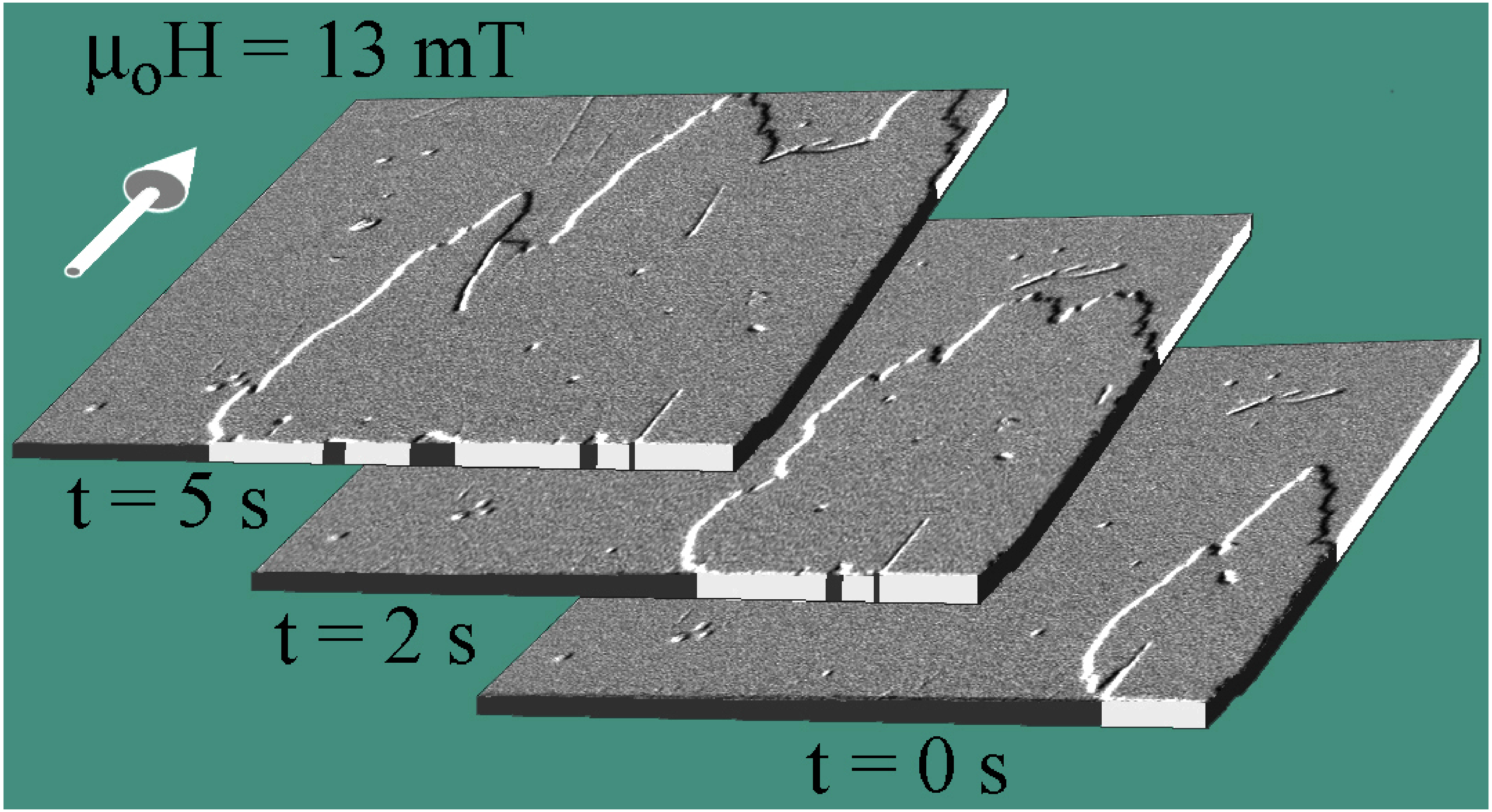


Results in
2 Time Constants!

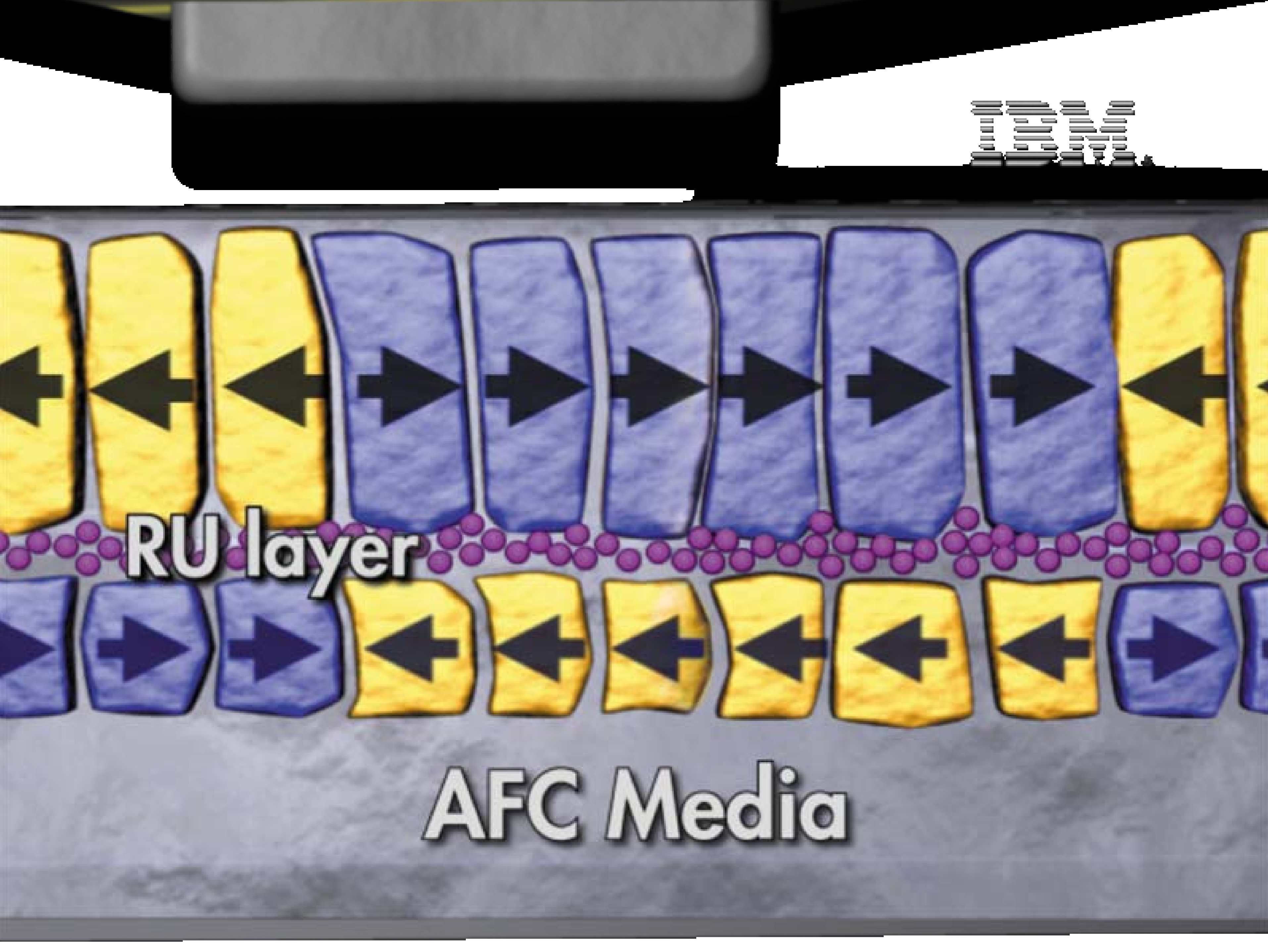


Two-Step Field-
Change Method

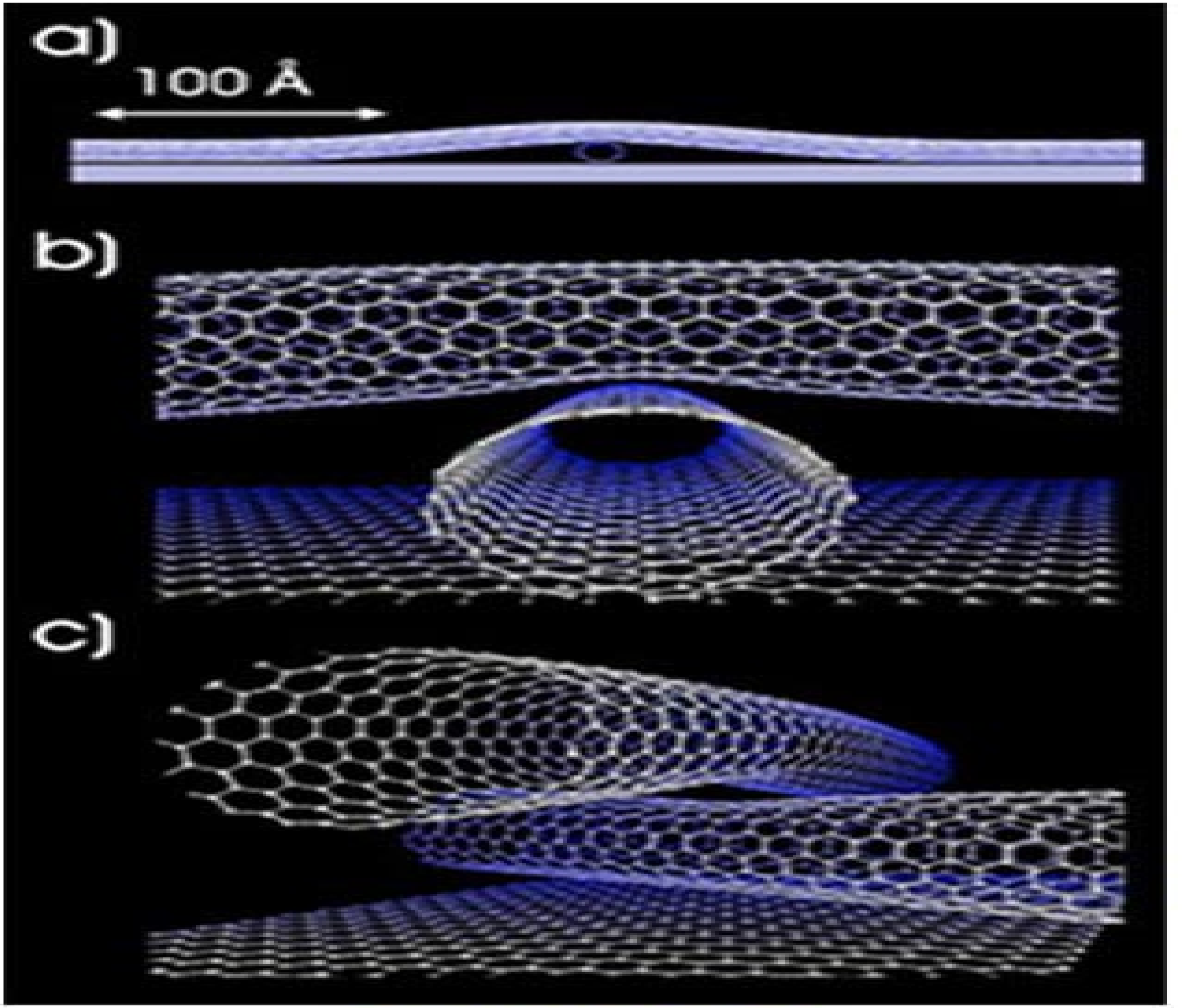
Time Dependent Domain Activity



Co(2.5 nm)/Ru(0.5 nm)/Co(2.1 nm) Synthetic AF Media


IBM
RU layer
AFC Media

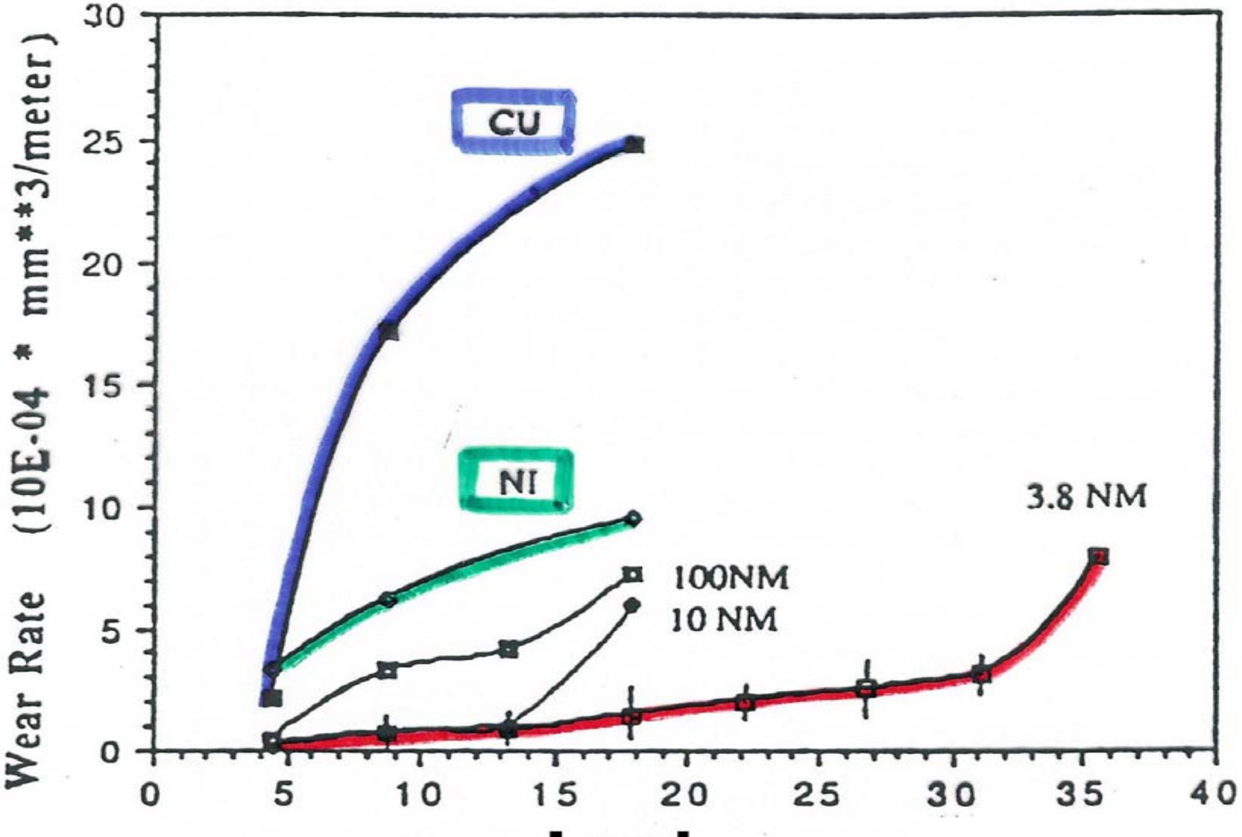
CARBON NANOTUBES



(Courtesy of IBM)

DECREASED WEAR RATE

(Cu/Ni Multilayers)



D.S. Lashmore & A.W. Ruff, Wear 151, 245 (1991).

DISLOCATIONS?

Hall-Petch

$$\sigma_y = \sigma_0 + k d^{-1/2}$$

Frank-Read Source

$$\tau \sim \frac{Gb}{l}$$

$\tau \to \infty$ as $l \to 0$

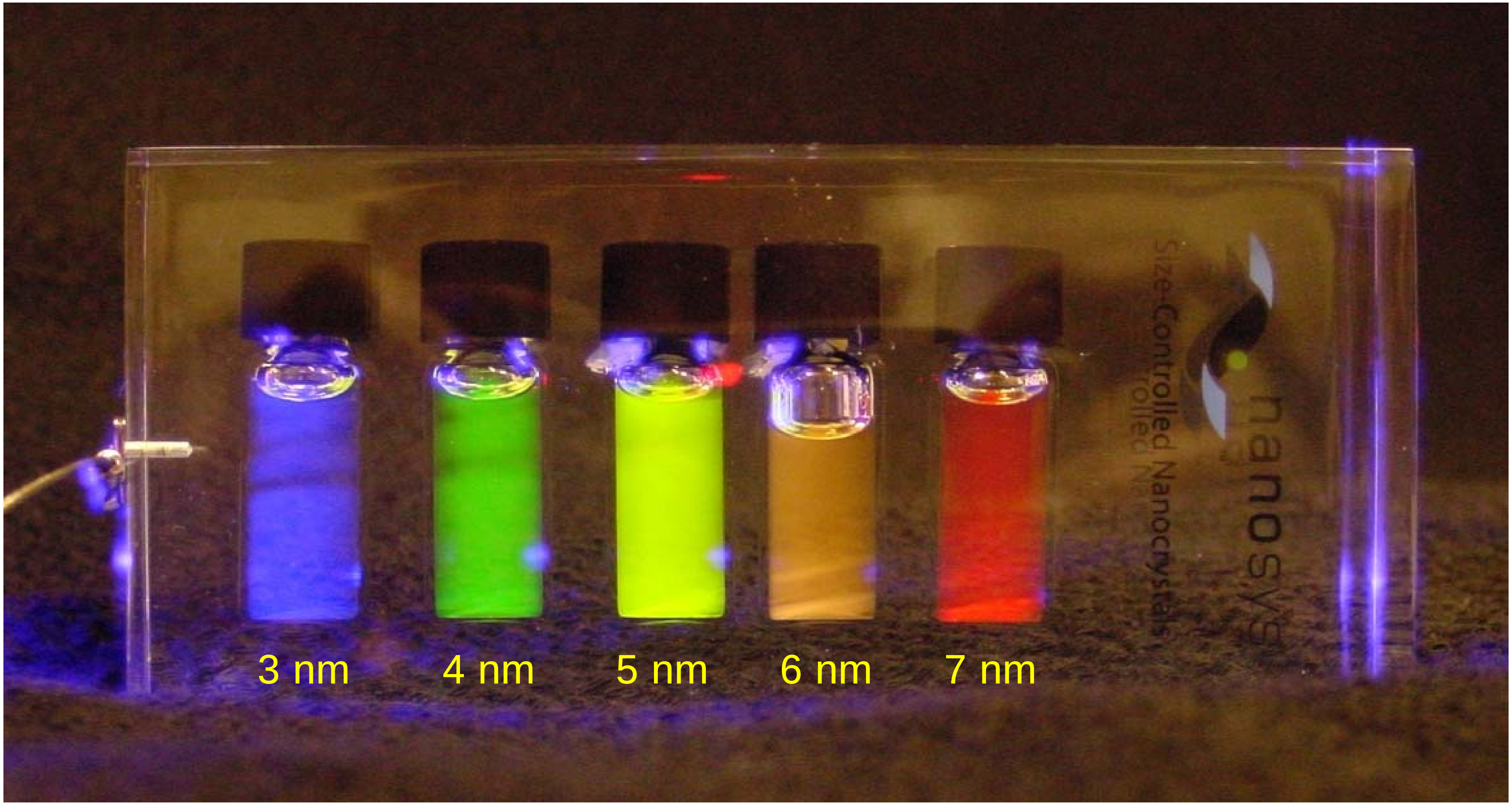
Image Forces

$$F = \frac{Gb^2}{4\pi(1-\nu)} \frac{1}{r}$$

← dist. from GB to dislocation

Unique Properties From Nanoscale Size

Illustration of Quantum Size Effect in Cadmium Selenide



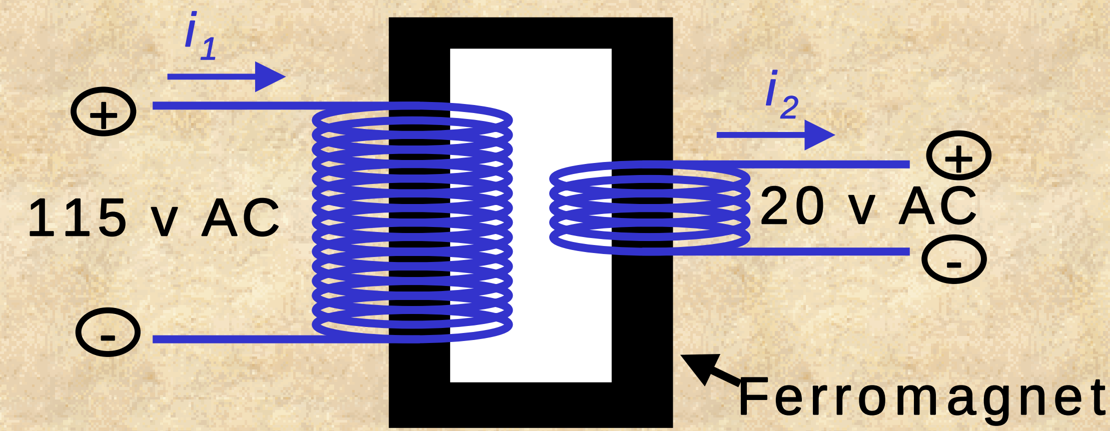
Color of fluorescence determined by size of particles and type of material

PARTICLE SIZE MEASUREMENT

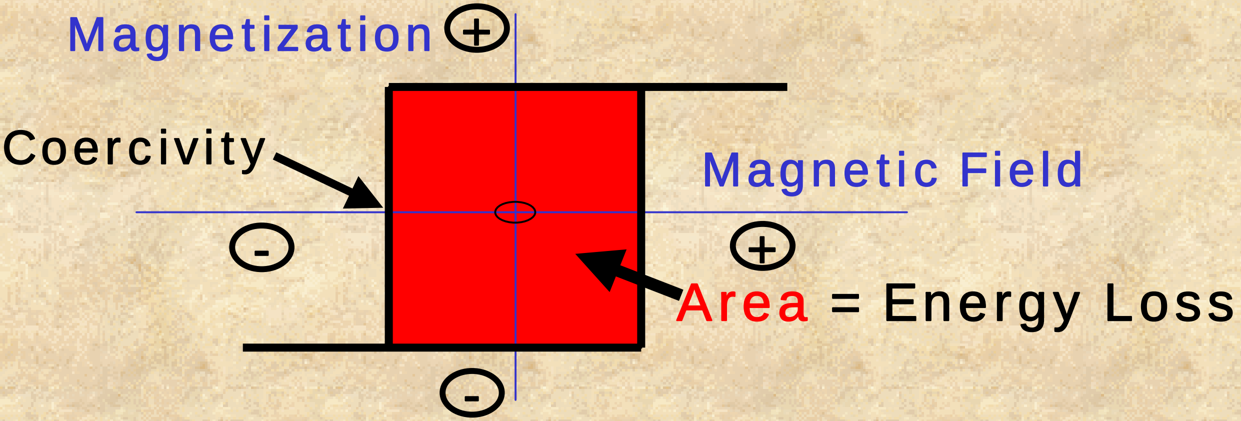
- X-Ray Diffraction: Scherer Formula
- X-Ray Diffraction: Warren-Averbach Method
- Dynamic Light Scattering
- Transmission Electron Microscopy
- Differential Mobility Analyzer
- Mass Spectroscopy: charge/mass ratio
- Gas Adsorption: BET Method

BUT THEY DON'T ALL AGREE !!!

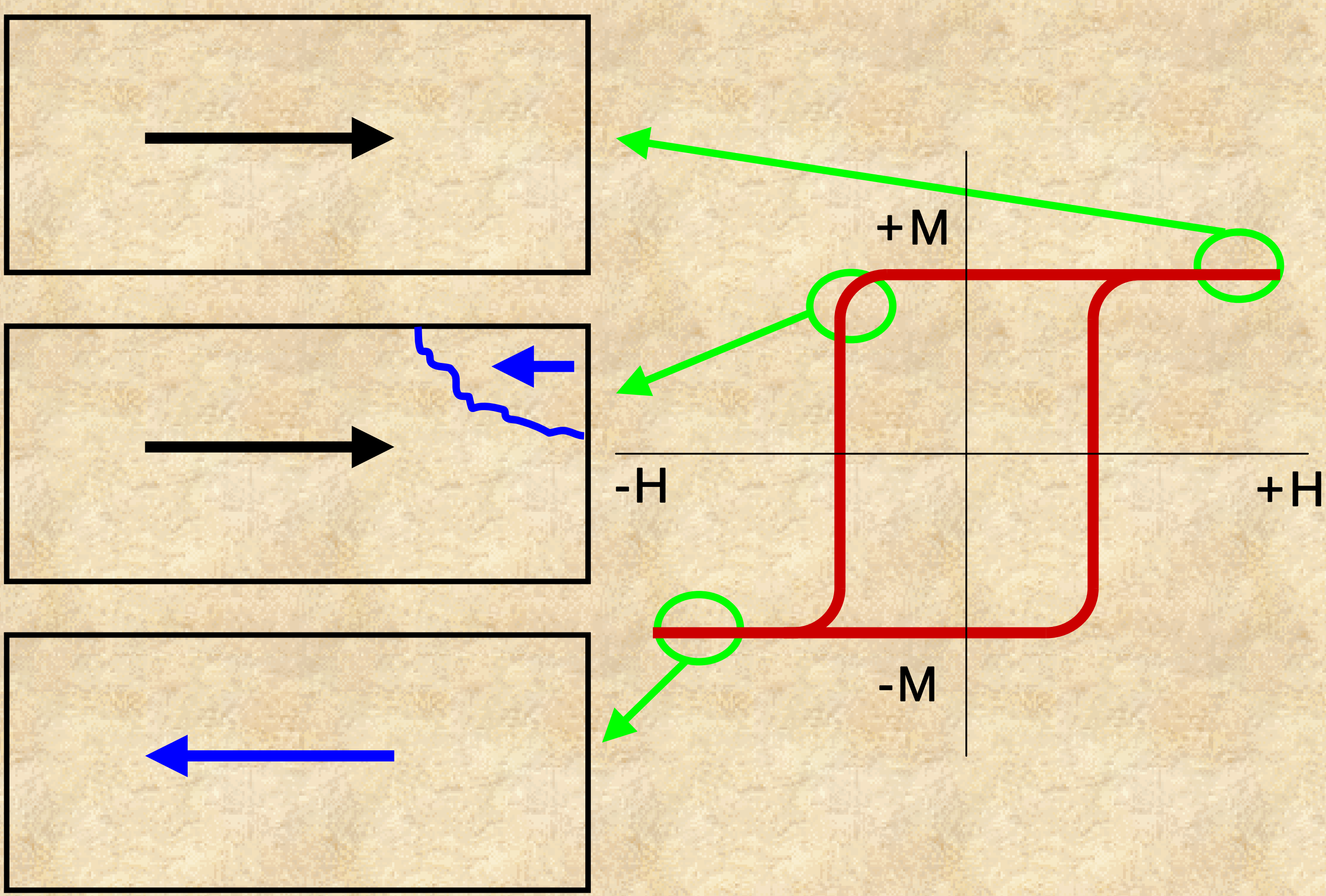
TRANSFORMER



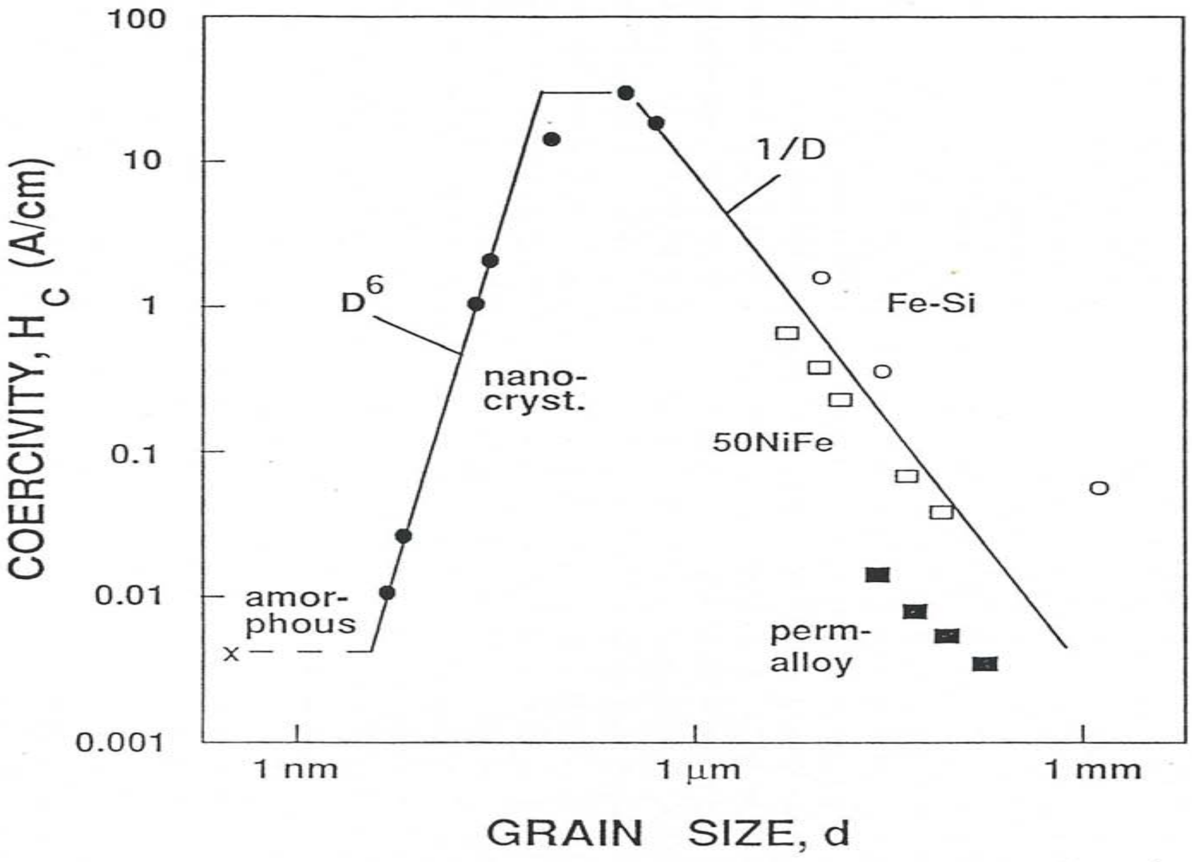
"Hysteresis Loop" of Ferromagnet



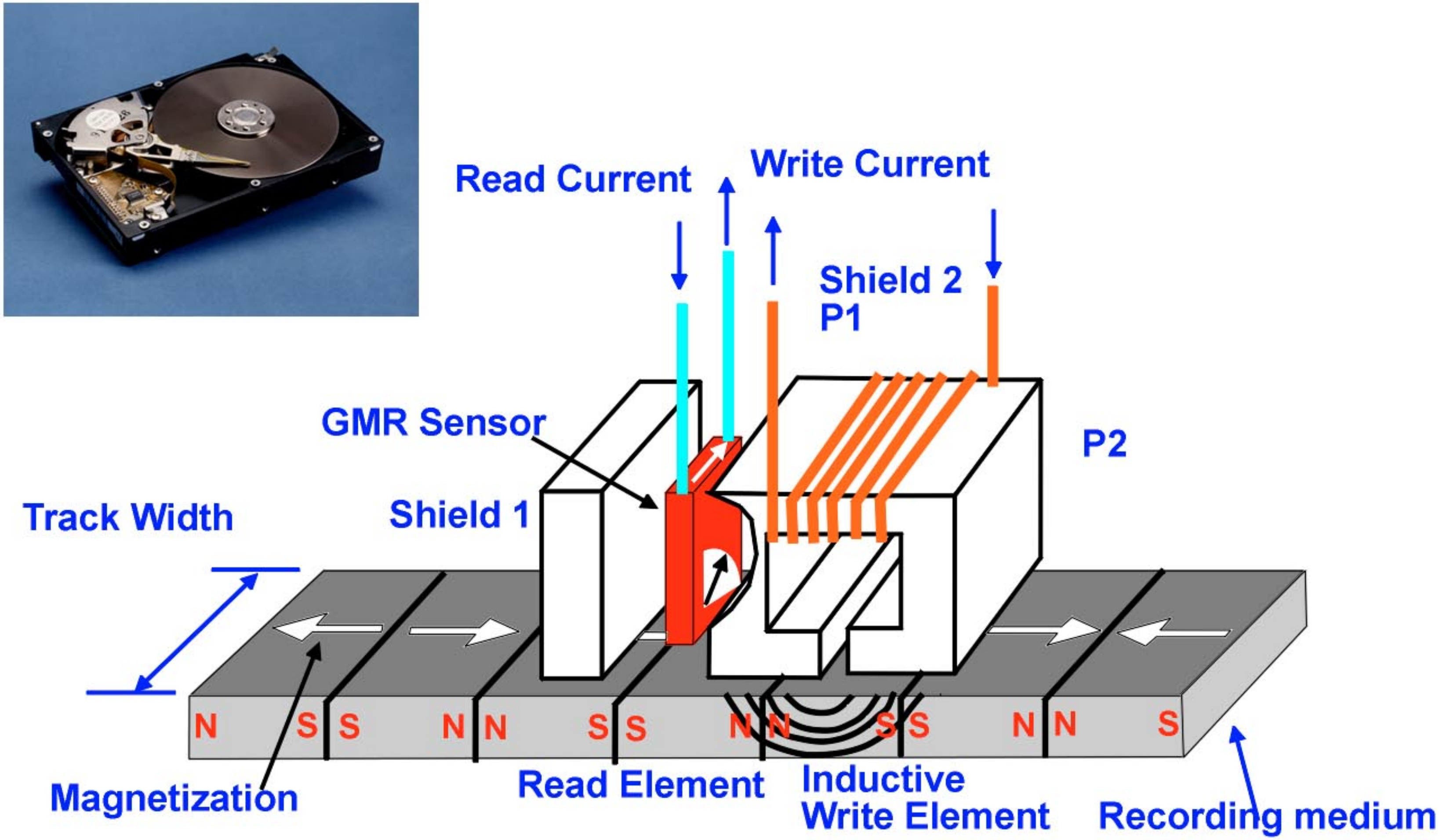
Magnetization Reversal by Domain Nucleation & Growth



ENHANCED (AND REDUCED) MAGNETIC COERCIVITY



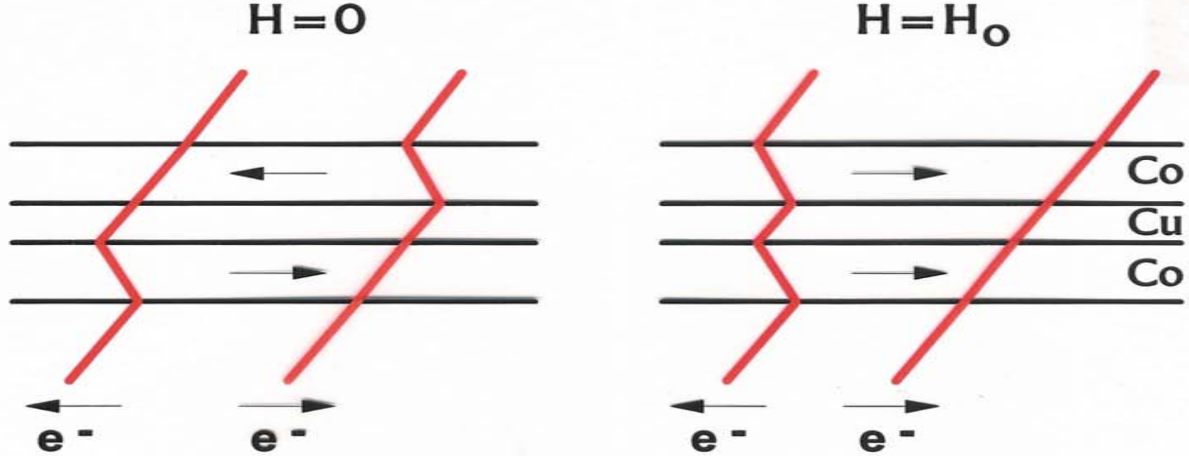
Magnetic coercivity vs. grain size for several soft ferromagnetic materials. [G. Herzer, IEEE Trans. MAG26, 1397 (1990)]



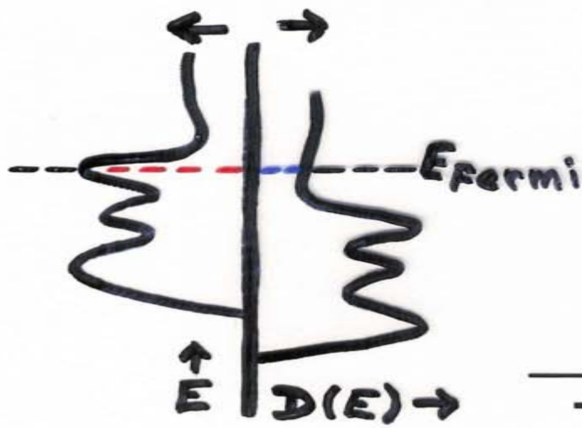
Magnetic recording process.

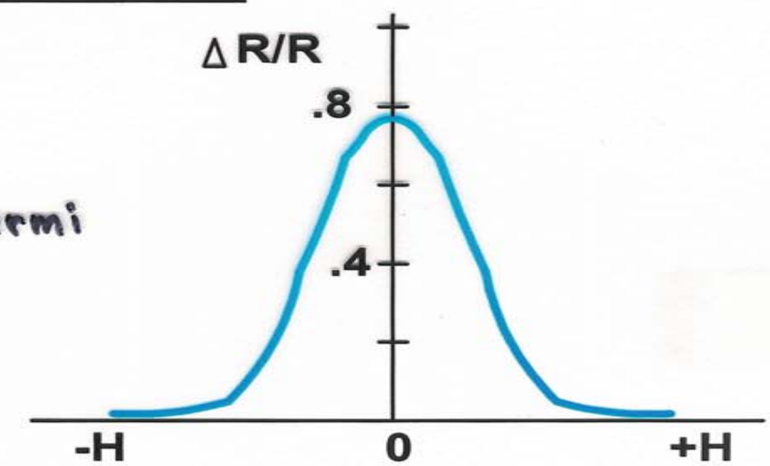
Ed Grochowski
IBM Almaden Research Center

GIANT MAGNETORESISTANCE FIELD SENSORS

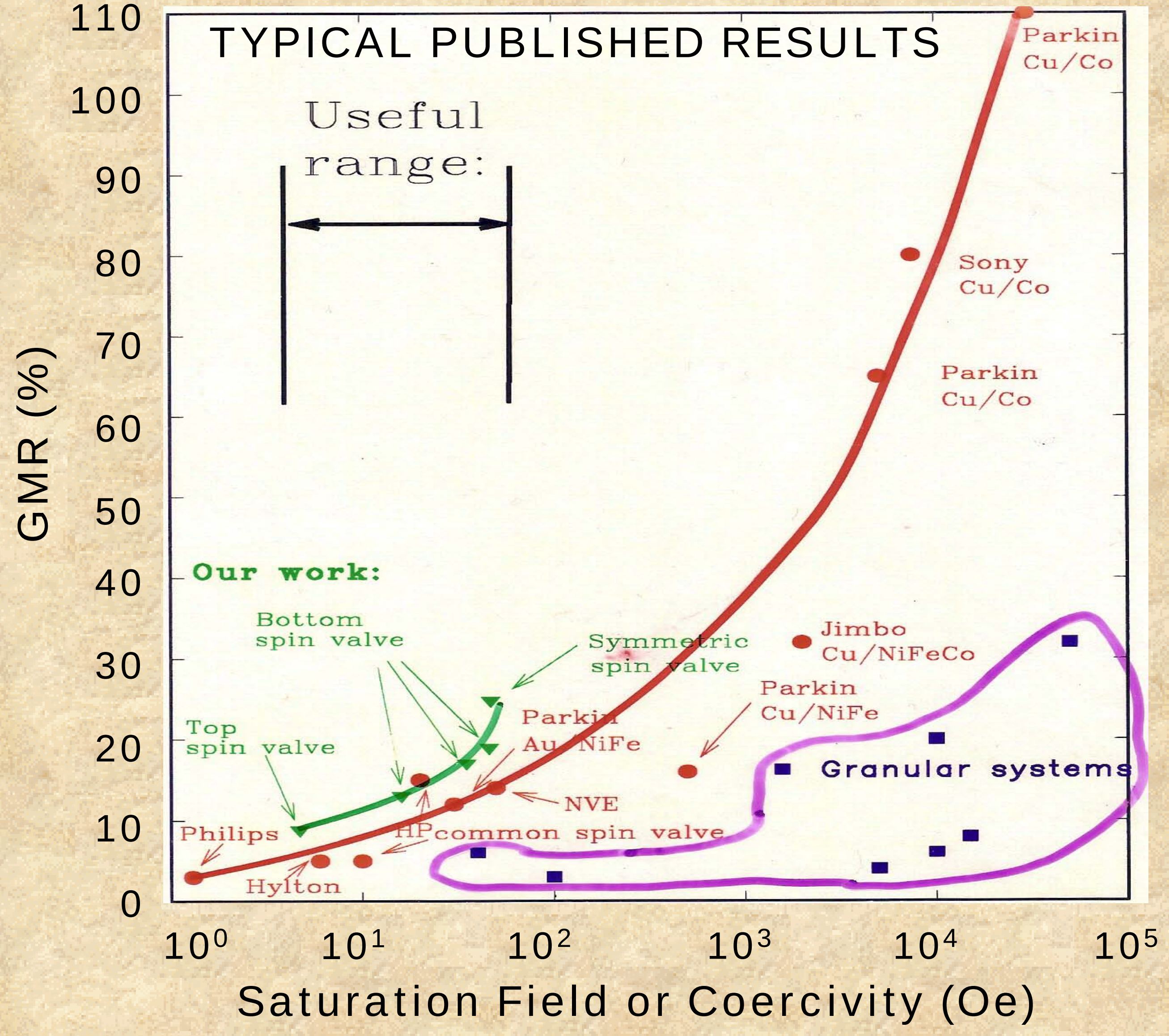


$$1/R = 1/\overleftarrow{R} + 1/\overrightarrow{R}$$



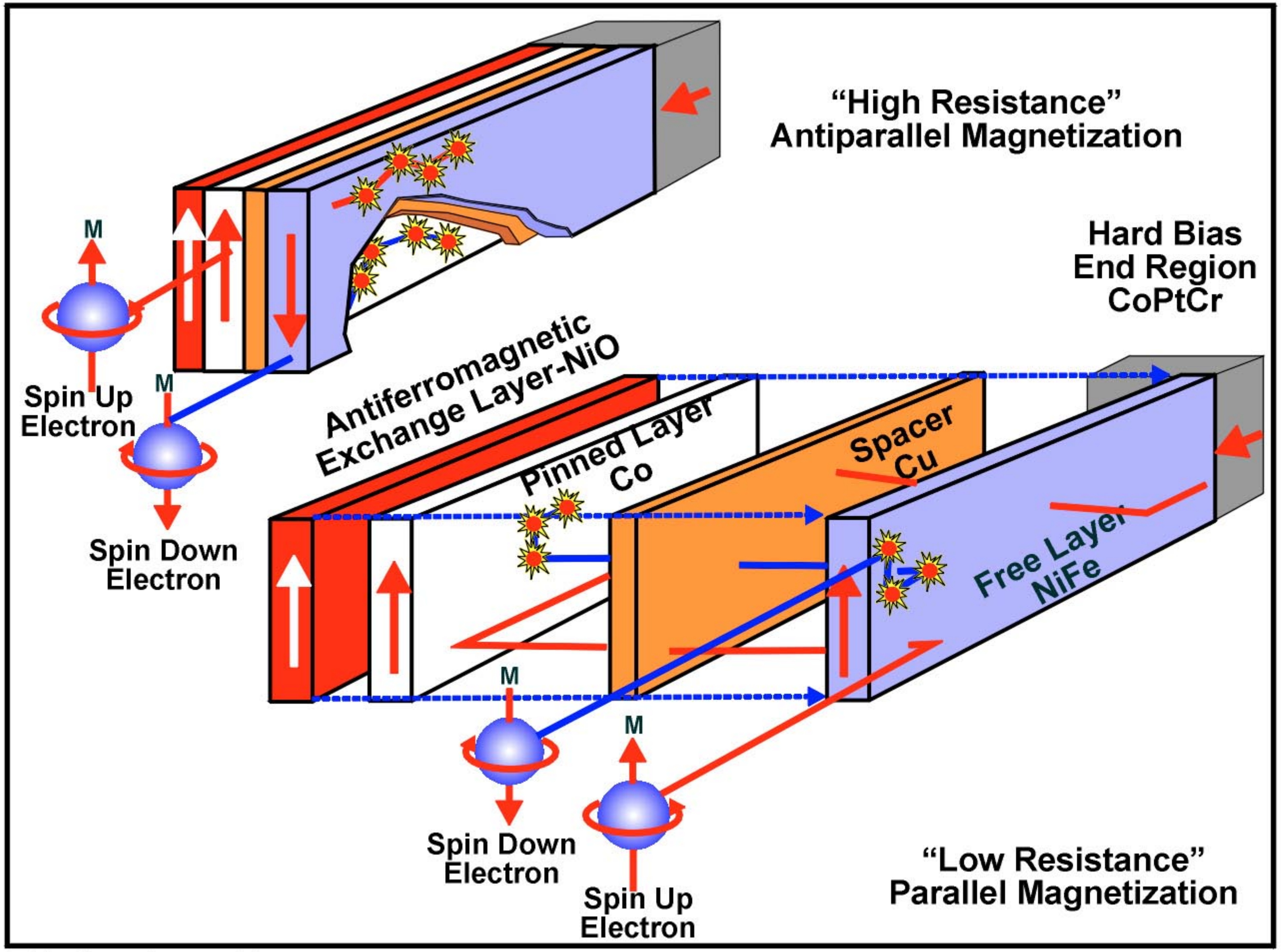


Magnetic Materials Group



National Institute of Standards and Technology

GMR/ Spin valve operation



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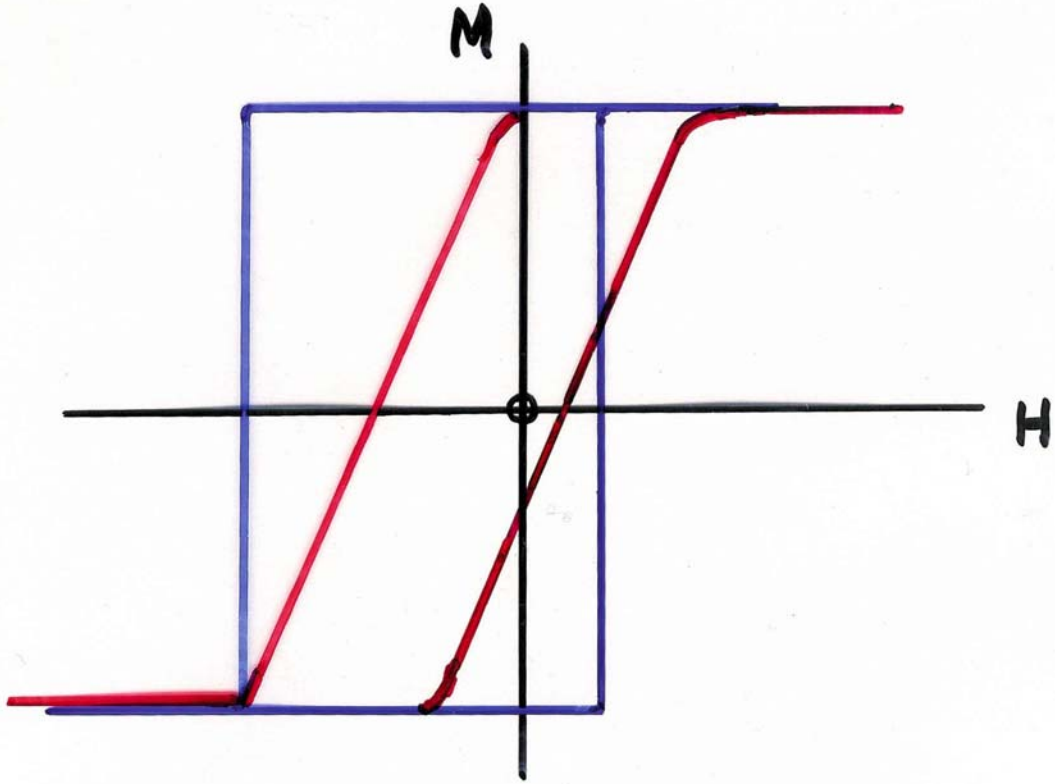
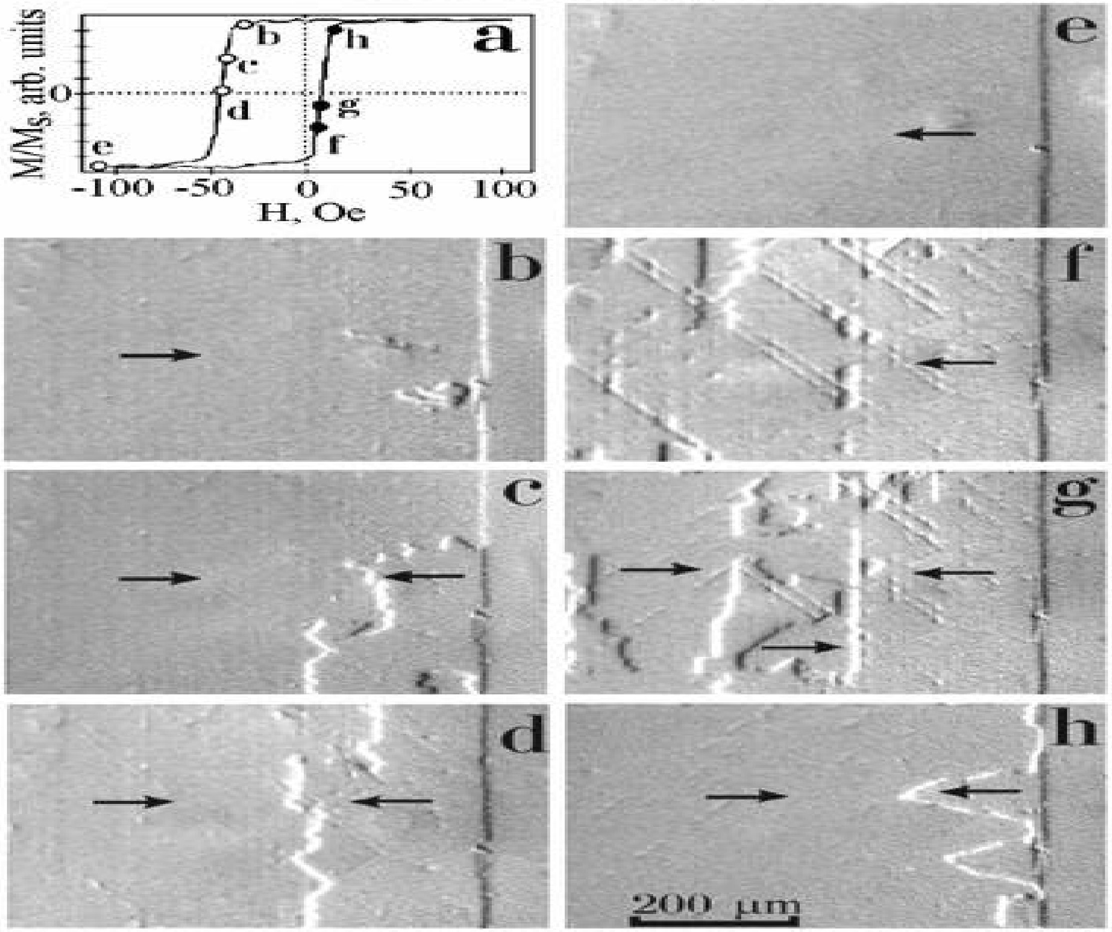
IBM Almaden Reseach Center

Exchange - Bias



Magnetic Materials Group

MOIF Images of the Remagnetization Process in an Exchange-Biased NiO/NiFe AF/FM Bilayer

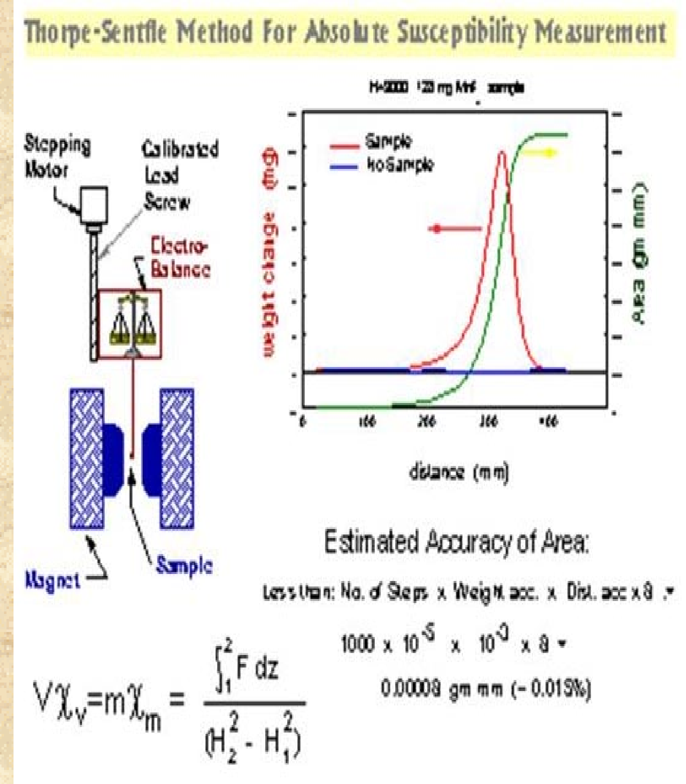


Nikitenko, Gornakov, Dedukh, Yu, Kabanov, Khapikov, Shapiro, Shull, Chaiken, Michel, PRB *57*, R8111 (1998).

National Institute of Standards and Technology

Magnetic Materials Group

ABSOLUTE MOMENT MAGNETOMETER

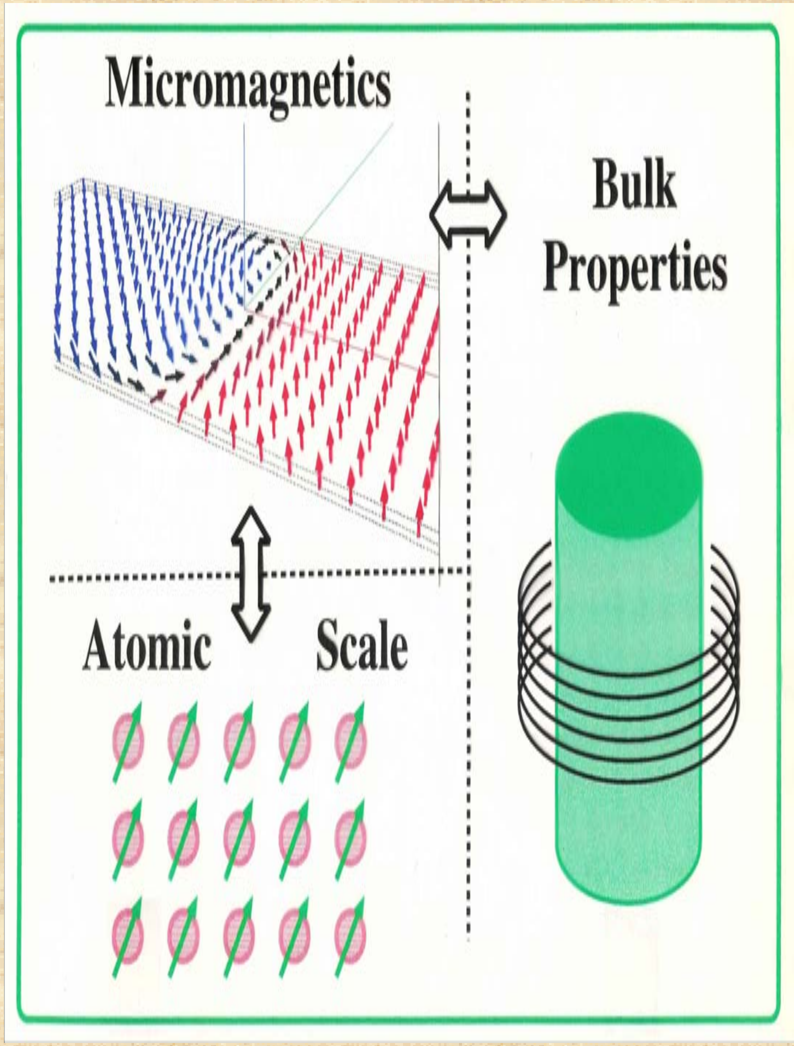


$$V\chi_v = m\chi_m = \frac{\int_1^2 F\,dz}{(H_2^2 - H_1^2)}$$

Certified Standards: (1) Ni Sphere, (2) Ni Disc, (3) YIG Sphere, (4) Pt Cylinder

NIST
National Institute of Standards and Technology

Computational Standards



Micromagnetic Equations

$$(1+\alpha^2)\frac{\partial \mathbf{M}}{\partial t} = -\gamma\,\mathbf{M}\times\mathbf{H}_{\text{eff}} - \frac{\gamma\alpha}{M_s}\mathbf{M}\times(\mathbf{M}\times\mathbf{H}_{\text{eff}})$$

$$\mathbf{H}_{\text{eff}} = -\partial\mathcal{E}_{\text{tot}}/\partial\mathbf{M}$$

$$\mathcal{E}_{\text{tot}} = \mathcal{E}_{\text{ex}} + \mathcal{E}_{\text{K}} + \mathcal{E}_{\text{s}} + \cdots$$

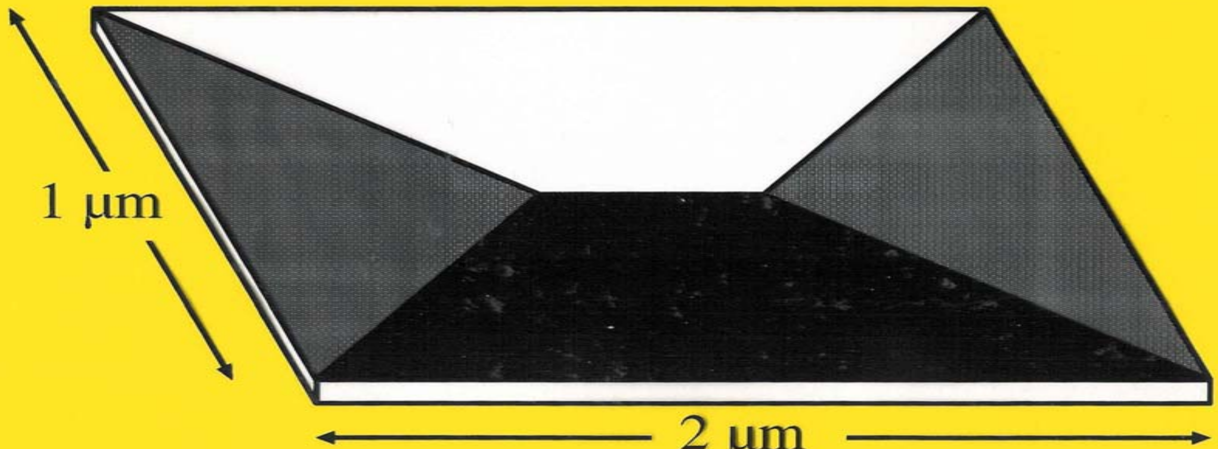
$$\mathcal{E}_{\text{ex}} = \frac{A}{M_s^2}\left[(\nabla M_x)^2 + (\nabla M_y)^2 + (\nabla M_z)^2\right]$$

$$\mathcal{E}_{\text{K}} = \frac{K_c}{M_s^4}(M_x^2 M_y^2 + M_y^2 M_z^2 + M_z^2 M_x^2)$$

$$\mathcal{E}_{\text{s}} = -\frac{1}{2}\mathbf{M}\cdot\int_V(\nabla\cdot\mathbf{M})G\,dv + \int_S \mathbf{M}\cdot\mathbf{n}G\,ds$$

Standard Problem #1

"Permalloy" rectangle



20 nm thick

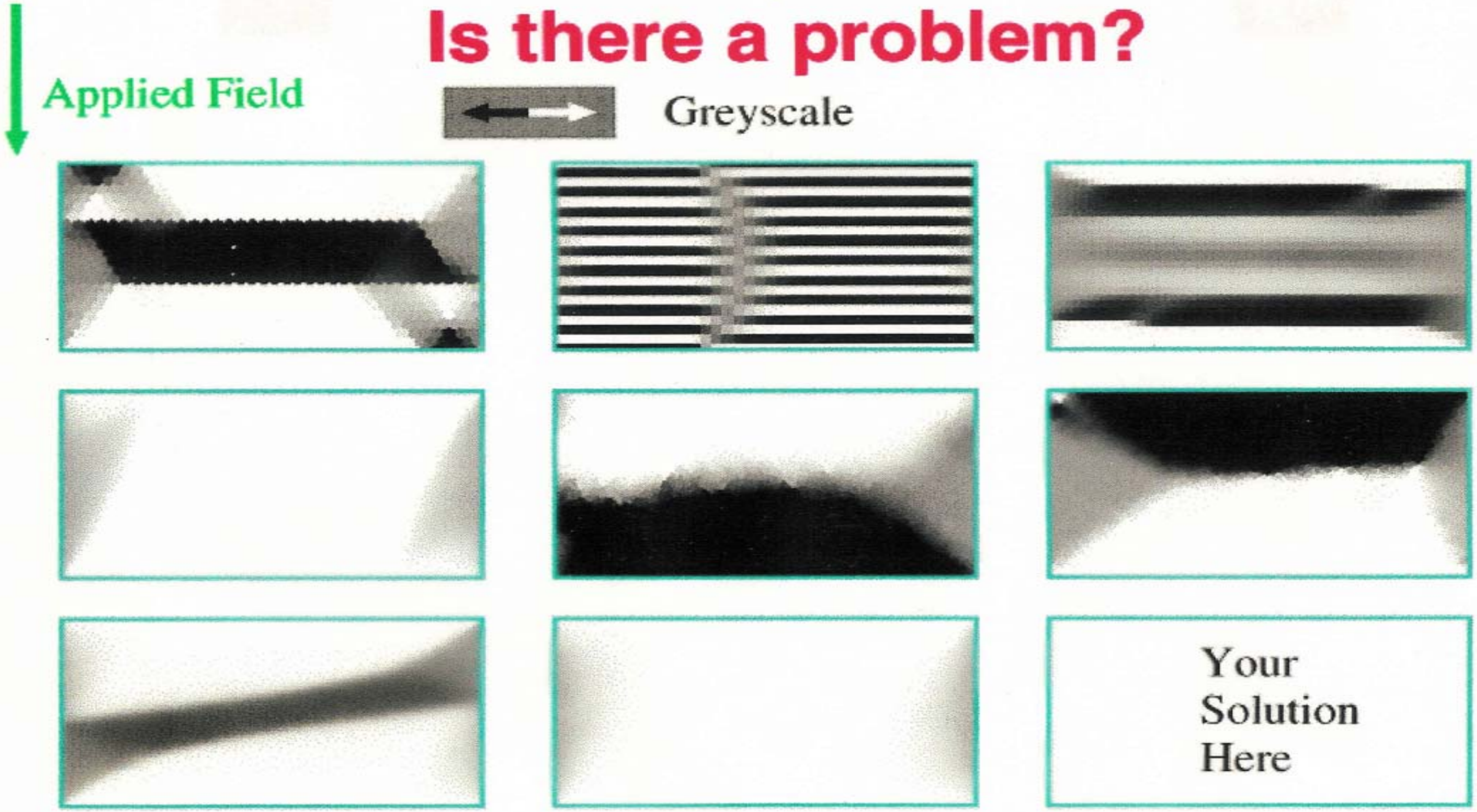
$A = 1.3\text{x}10^{-11}$ J/m ($1.3\text{x}10^{-6}$ erg/cm)

$M = 8.0\text{x}10^{-5}$ A/m (800 emu/cm^3)

$K = 500$ J/m^3 (5000 erg/cm^3)

Standard Problem #1, Round Robin Results:

Is there a problem?



Yes.

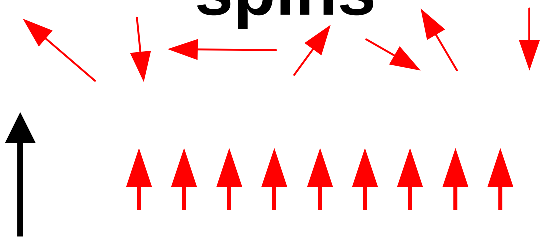
MAGNETOCALORIC EFFECT

SYSTEM = SPIN + LATTICE

spins | lattice

at H = 0 | $T = T_0$

at $H = H_{Appl}$ | $T = T_1$



Total entropy change of the (Spin+Lattice) system upon application of a magnetic field, H_{Appl}, (reversibly) is ZERO.

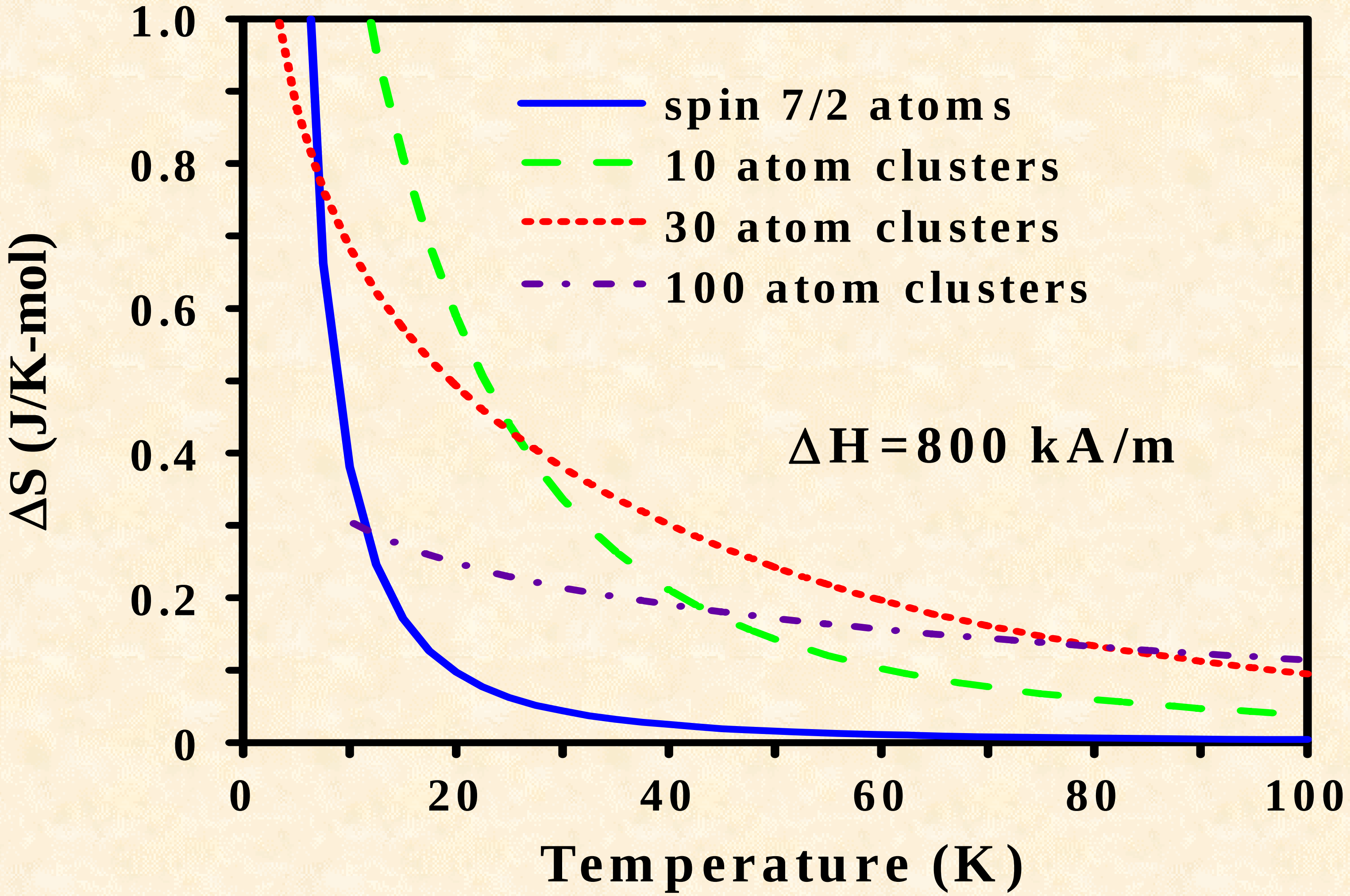
Decrease in spin entropy causes an increase in lattice entropy, $C_H dT/T$.

Magnetocaloric effect = dT = $(T_1 - T_0)$.

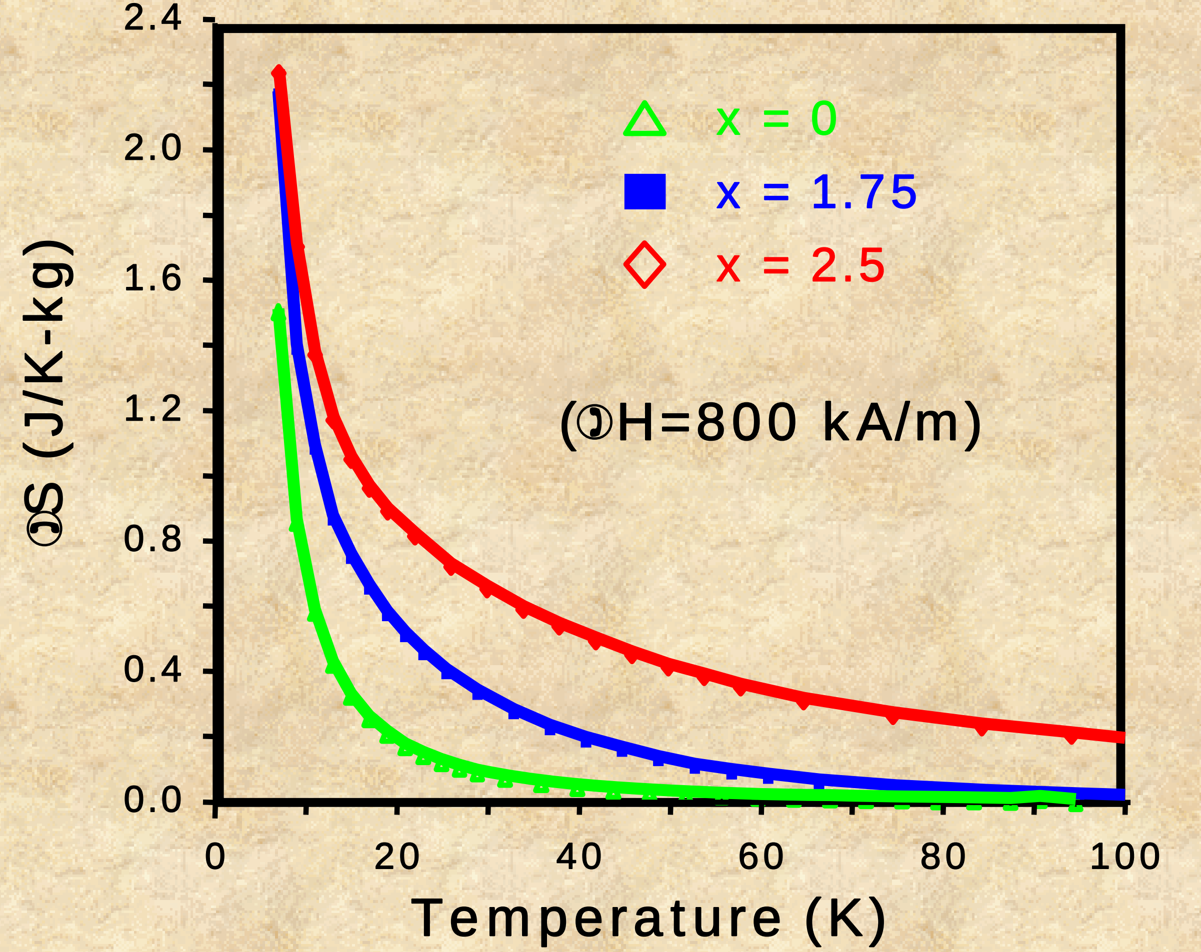
WHY MAGNETIC REFRIGERATORS ???

- Large Entropy Change on Ordering
  (40-200 times that of a gas)
- Based on a REVERSIBLE Process
  (Carnot efficiencies conceivable)
- Refrigerant and Heat Transfer Media are
  DIFFERENT (No chlorofluorocarbons, CFCs)
- No Compressor & Few Moving Parts
  (Low vibration, High durability)

Entropy Enhancement in Nanocomposites



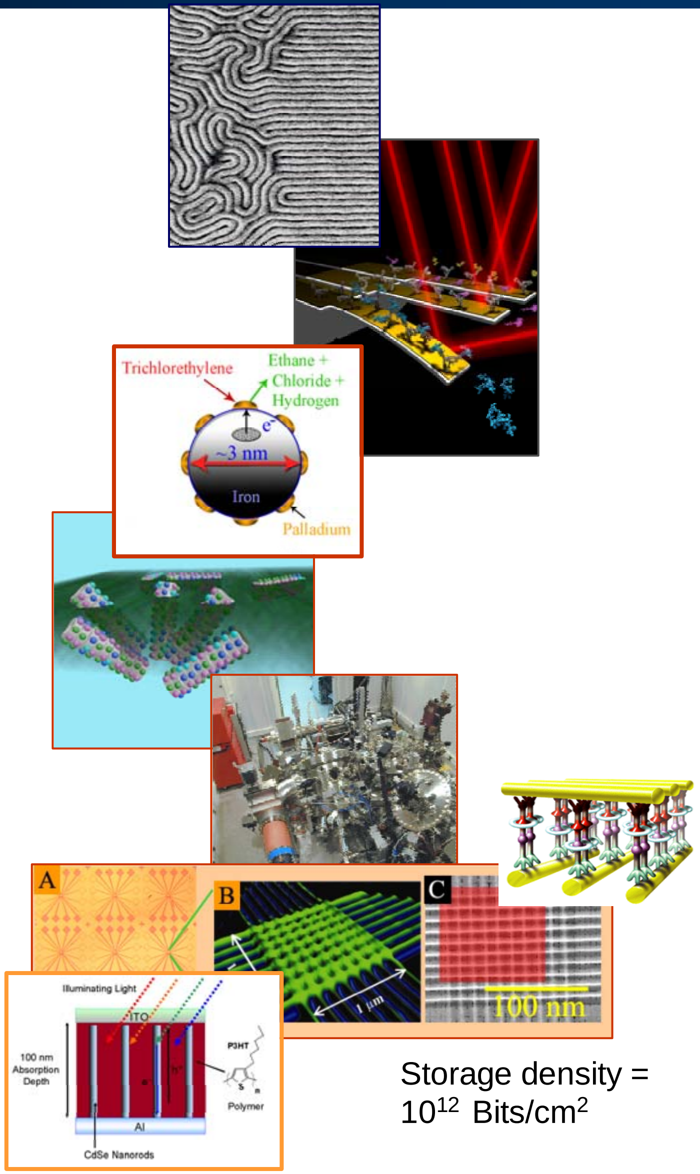
Magnetocaloric Effect Entropy Changes for $Gd_3Ga_{5-x}Fe_xO_{12}$ Nanocomposites



R. McMichael, J. Ritter, R. Shull, J. Appl. Phys. 73, 6946 (1990).

NNI Grand Challenge Areas

- Chemical-Biological-Radiological-Explosive Detection and Protection 5/02
- Nanostructured Materials by Design 6/03
- Manufacturing at the Nanoscale 2/03
- Nanoscale Processes for Environmental Improvement 5/03
- Healthcare, Therapeutics and Diagnostics 10/03
- Nanoscale Instrumentation and Metrology 1/04
- Nano-Electronics, Photonics and Magnetics 2/04
- Efficient Energy Conversion and Storage 3/04
- Space Exploration 8/04



Storage density = 10^{12} Bits/cm^2

Grand Challenge Workshop on Instrumentation and Metrology

Dr. Robert D. Shull

Materials Science & Engineering Engineering Laboratory

National Institute of Standards and Technology

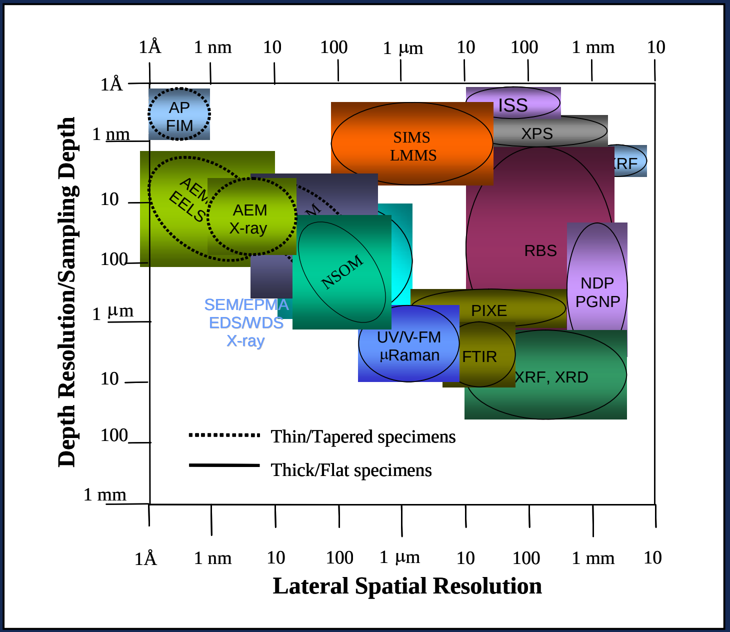
January 27-29, 2004

Breakout Session Focus Topics

- Nanocharacterization (physical and chemical properties, structures)
- Nanomechanics (mechanical properties, tribology)
- Nanoelectronics, nanomagnetics, and nanophotonics (device performance and materials properties)
- Nanofabrication (instrumentation for nanofabricated structures, devices)
- Nanomanufacturing (mass production, fast measurement technology for production applications)
- Crosscutting - Computational

State-of-the-Art in the Field

- The current state-of-the-art often reflects a trade off between one metrology need at the expense of another.
  – To establish the extent of chemical heterogeneity within a sample, one may have to accept something less than a Cartesian coordinate known to +/- 0.01 nm for each of the atoms that constitute the sample.



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•Similarly, the size and complexity of a structure that can be mapped may reflect a trade off in time spent on the analysis and the detection limit that is realized.

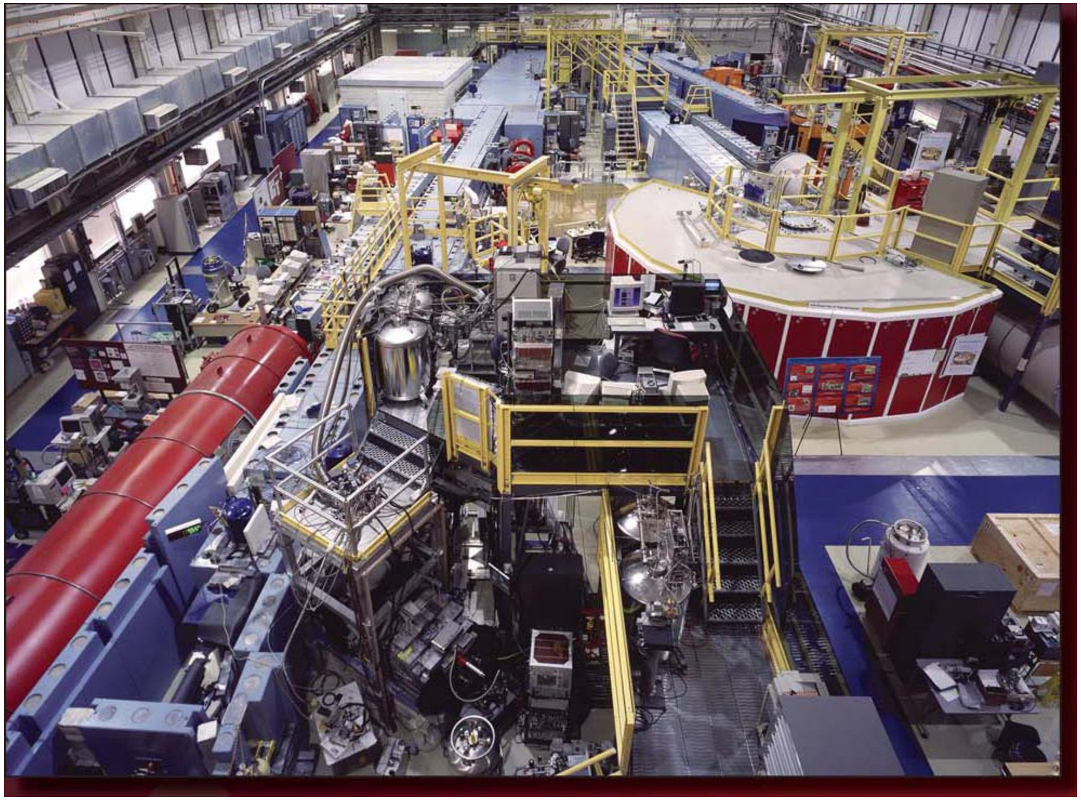
Grand Challenge: Instrumentation and Metrology

- ***To develop the ability to image and/or measure any nanostructure for any relevant property in 3-dimensions with atomic accuracy.***
- ***This requires the development of new metrology instrumentation and infrastructure for both laboratory research and nanomanufacturing.***

Workshop Conclusions

- *Revolutionary rather than evolutionary advances are needed*
- *Current semiconductor instrumentation is of limited usefulness*
- *Funding is needed for educational programs to upgrade university facilities and to create a multi-disciplinary research community for metrology at the nanoscale.*
- *Entirely new metrology tools are needed*

NIST Center for Neutron Research



- 29 experiment stations
- www.ncnr.nist.gov
- Operated as a major national user facility
- Merit-based access made available to the entire U.S. technological community
- Each year, over 1700 research participants use the facility for measurements

ity


Nanomagnetics

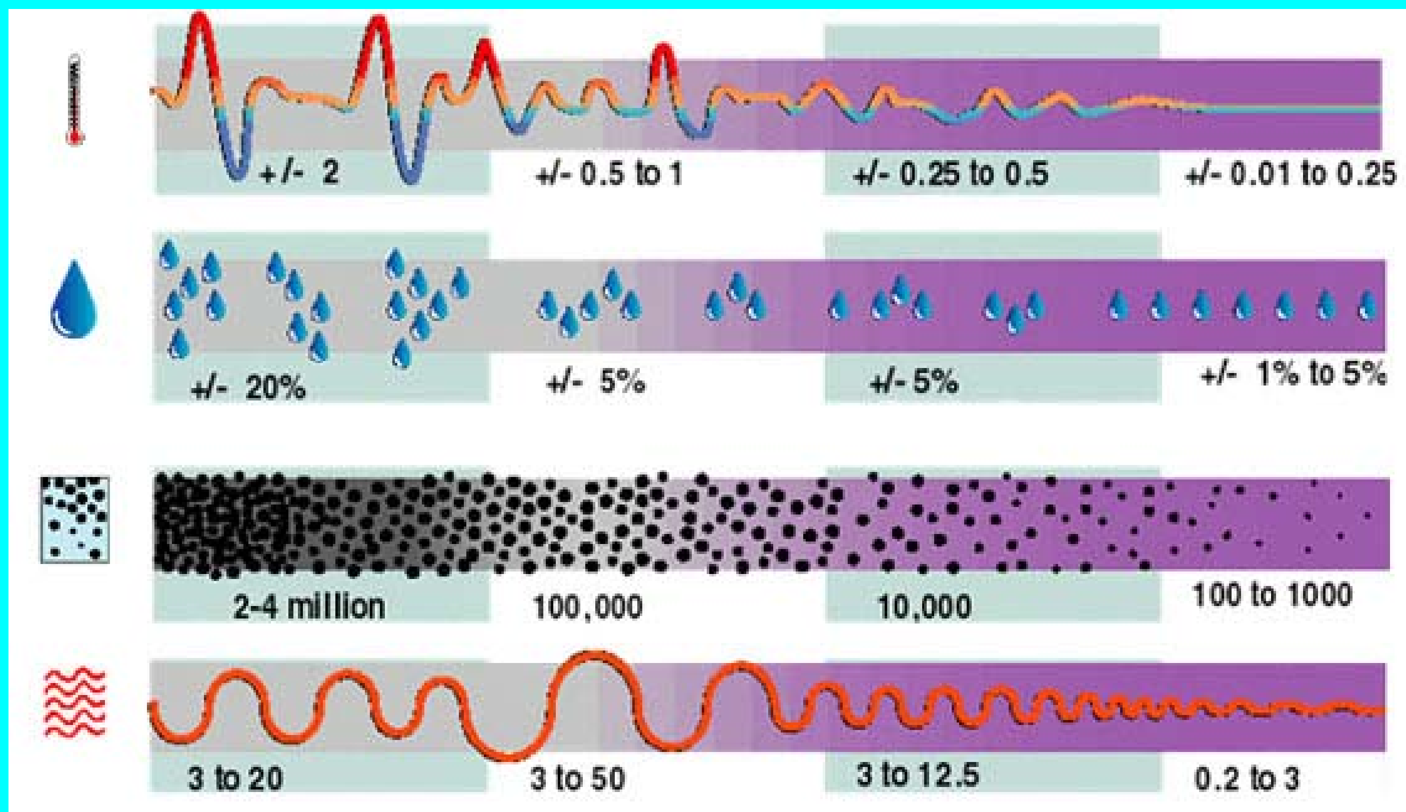

Molecular Measuring Machine

logy research facility

(air quality, temperature, vibration, humidity)

Critical Criteria - NIST AML

- Developed for advanced nanometrology
- Designed to be the most environmentally stable laboratory in the world.



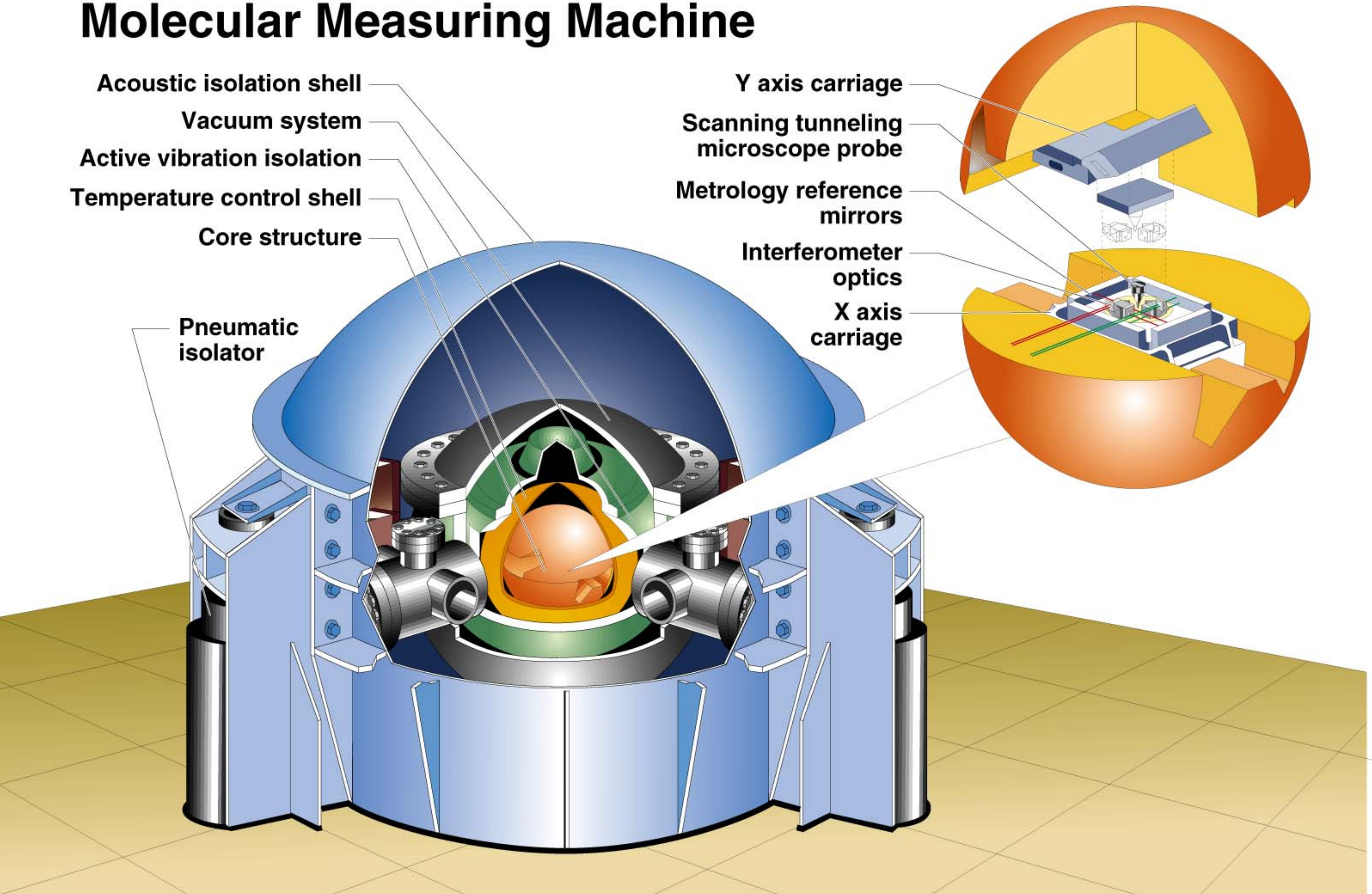
	Current NIST Facilities	Modern Laboratories	Renovated NIST Labs	NIST AML Criteria
Temperature Control +/- 0.01 Degrees Celsius	+/- 2	+/- 0.5 to 1	+/- 0.25 to 0.5	+/- 0.01 to 0.25
Humidity Control +/- 1 %	+/- 20%	+/- 5%	+/- 5%	+/- 1% to 5%
Air Quality Class 100 - M3.5	2-4 million	100,000	10,000	100 to 1000
Vibration Control 0.2 - 3 Micrometers/second	3 to 20	3 to 50	3 to 12.5	0.2 to 3

State-of-the-Art & Next-Generation Measurement Capabilities to be Housed in the AML

Over 100 experiments are being moved into the AML

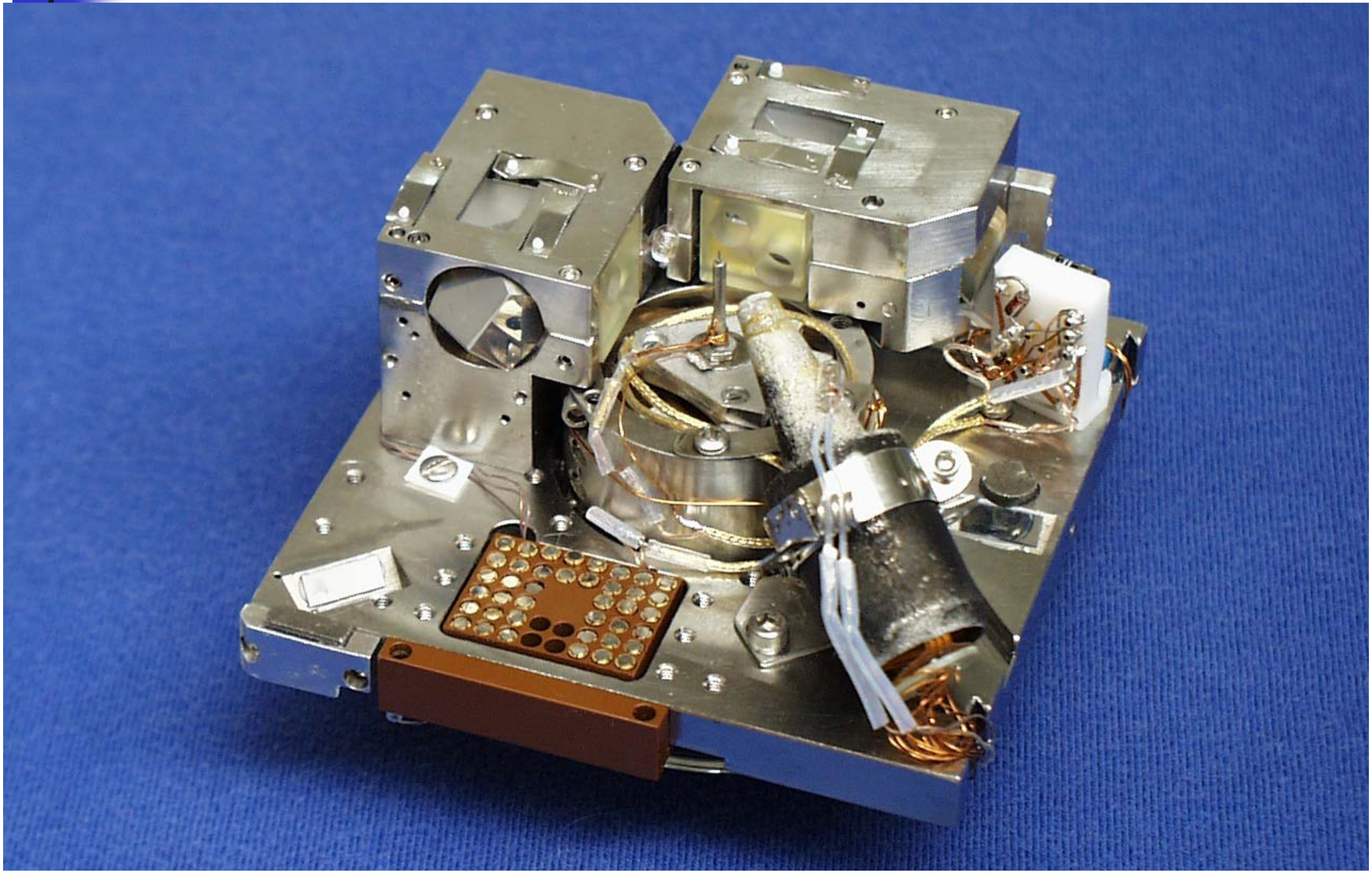
- Improved Standards Capabilities for next generation nanometrology requirements
  - Length standards ranging from nano to meso-scale
  - Mass, vibration, and pressure standards
  - Fundamental electrical standards
  - Optical and x-ray measurements and standards
- Chemical and physical characterization of three dimensional nano-scale structures and interfaces
- Imaging, characterization, and manipulation of matter at nano-scale, single atom, and molecular regimes
- Quantum information processing, advanced electron beam metrology instrument, optical tweezers, and Bose Einstein condensation

Molecular Measuring Machine

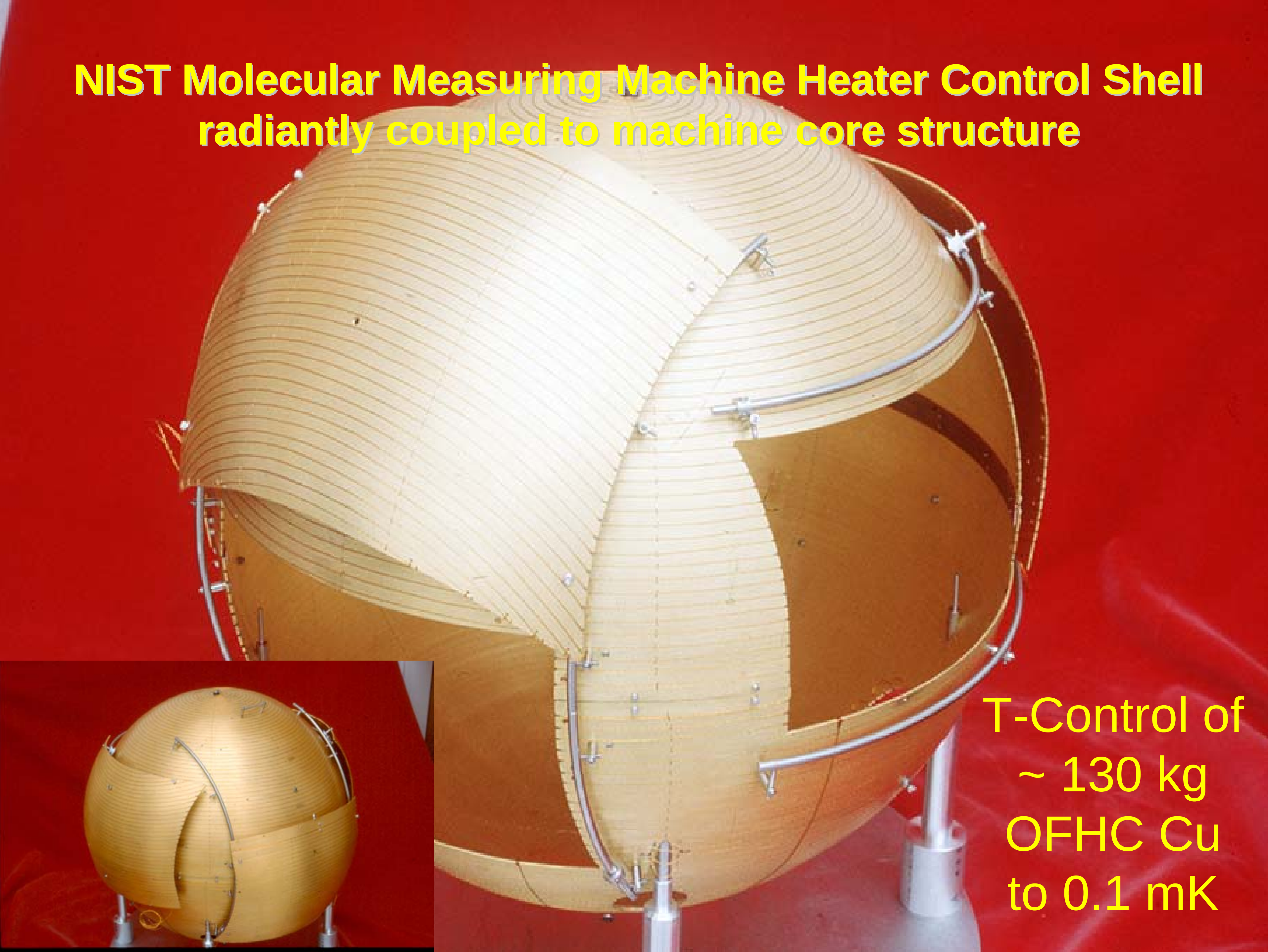


Measures location to 1 nm over a 5 cm x 5 cm area

M-cubed Probe and Interferometer Optics



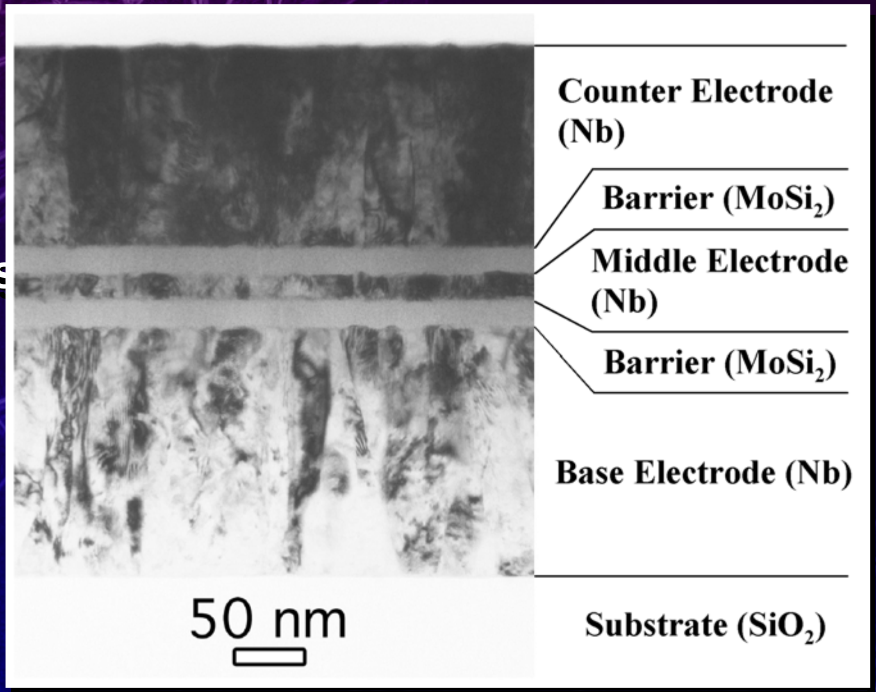
NIST Molecular Measuring Machine Heater Control Shell radiantly coupled to machine core structure

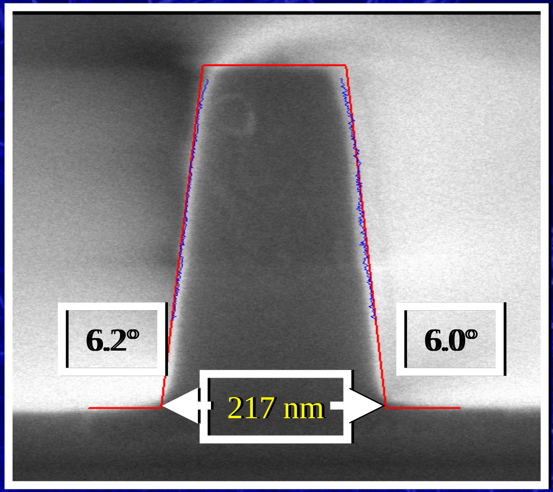


T-Control of
~ 130 kg
OFHC Cu
to 0.1 mK

Nanoelectronics

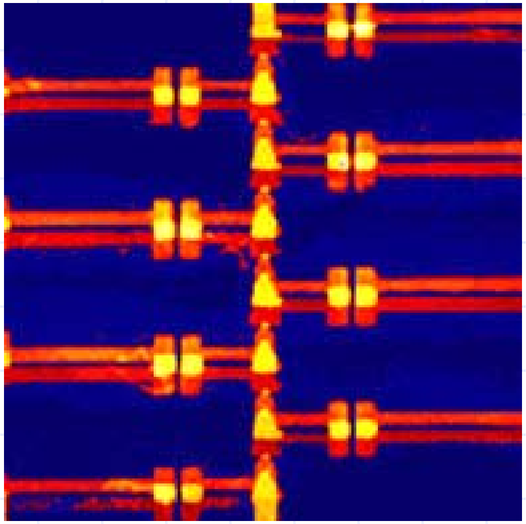
- High precision electrical metrology
  - Nano-stacks of Josephson junctions for new voltage standards.
- Accurate dimensional metrology
  - Model-based metrology work for accurate measurements of nanometer-sized structures in scanning electron microscopes
    - Being implemented in commercial instrumentation
    - 2004 SPIE Diana Nyyssonen Memorial Award





Fundamental Nanometrology

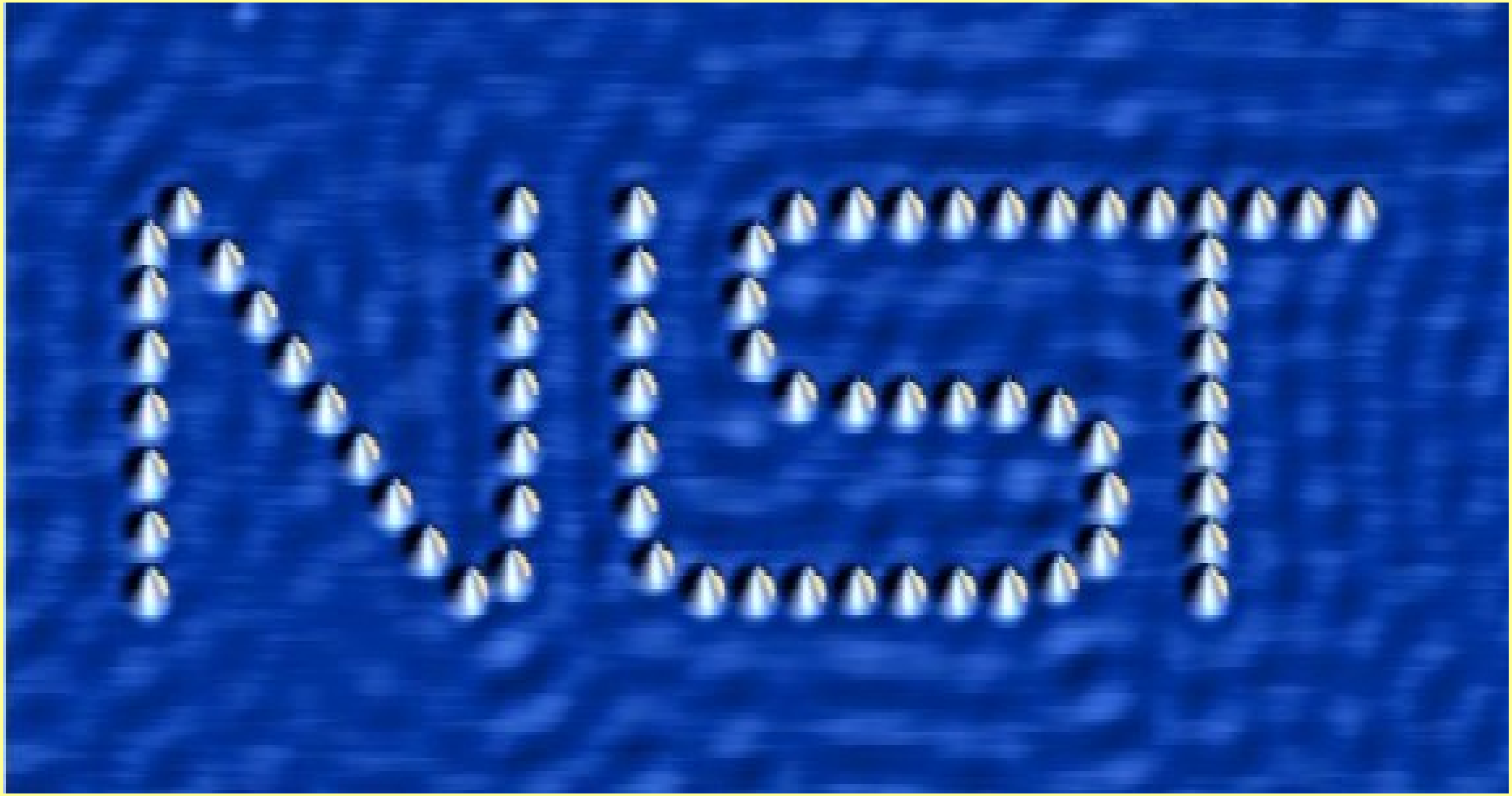
- High Precision Electrical Metrology
- NIST metrology work:
  - Single electron-tunneling based technologies
  - Fundamental representation of electrical quantities
  - Capacitance standard by counting the number of electrons in a nanocircuit
  - Quantum current standard under development



Nanocircuit that pumps one electron at a time to a capacitor

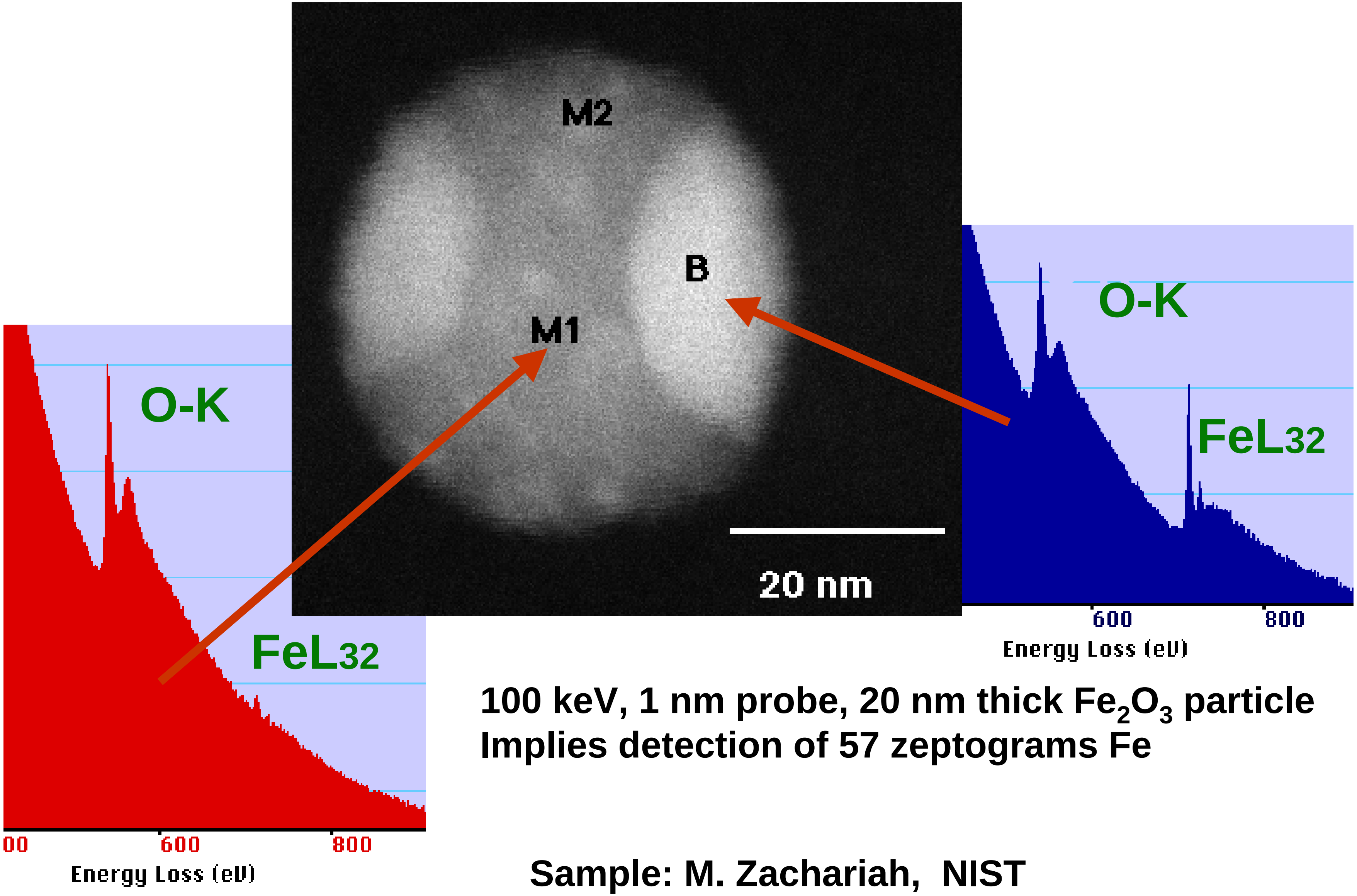
- Recent Accomplishment:
  - Determined capacitance standard can be run in a compact, transportable refrigerator
  - Quantified error mechanism for standard – predict precision of one part in 10^7

Nanoscale Physics Laboratory



Single Atom Positioning

Flame Synthesized SiO_2-Fe_2O_3



100 keV, 1 nm probe, 20 nm thick Fe_2O_3 particle
Implies detection of 57 zeptograms Fe

Sample: M. Zachariah, NIST
Analysis: D. Newbury, NIST

SUMMARY

- Nanometrology transcends all activity areas
- Nanometrology is NOT just the measurement of small lengths
- More sensitive detection is required since property values decrease with size
- New meas. methods for new properties needed
- New Instrumentation is needed
- New fabrication science needs developing
- Standards will be critical